Appendix 2.3 A

Task 2.3A: Solids Removal Technologies

Submitted by:

Christopher J. Gabelich, Tae I. Yun, and James F. Green

Metropolitan Water District of Southern California
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PREFACE

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What follows is the final report for *Electrotechnology Applications for Potable Water Production and Protection of the Environment,* Contract No. 500-97-044**,** conducted by the Metropolitan Water District of Southern California. The report is entitled "Electrotechnology Applications for Potable Water Production and Protection of the Environment: Task 3 Solids Removal Technologies." This project contributes to the Industrial/Agricultural/Water End-Use Energy Efficiency area.

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EXECUTIVE SUMMARY

Introduction

The practice of importing water into southern California, most notably from the Colorado River, has created a salt imbalance problem. Recent studies have shown that through the use of Colorado River water, approximately $95 million per year in damages are incurred to the public and private sectors for every 100 mg/L of TDS over 500 mg/L—the U.S. Environmental Protection Agency's secondary, non-health standard for TDS. In order to offset these societal costs and provide a reliable supply of safe and aesthetically pleasing water, the Metropolitan Water District of Southern California (Metropolitan) is evaluating new and promising water treatment technologies. One option to accomplish this goal is through desalination.

This project was conducted by Metropolitan to investigate various pretreatment technologies for use with Colorado River water desalination. Pretreatment technologies investigated included conventional treatment (coagulation, flocculation, sedimentation, multi-media filtration); conventional treatment with ozone disinfection and biofiltration; and microfiltration. This research will assist municipalities to minimize the cost of salinity reduction and may also be applicable to other surface water supplies.

Background

While the growing consensus of water treatment professionals is towards replacing aging conventional treatment plants with membrane filtration systems, one of Metropolitan's research goals is to determine if conventional treatment can serve as the pretreatment to a desalting facility in a cost-effective manner. Metropolitan's existing conventional treatment plants have been successfully operated for over 60 years; however they do not provide for any reduction in salinity. Since conventional treatment facilities at Metropolitan are already in place, significant savings could be realized by avoiding microfiltration (MF) and ultrafiltration (UF) pretreatment. This alone could reduce overall surface water desalination costs by about 17 percent.

Project Objectives

The objectives of this task were:

1. Evaluate pilot-scale conventional treatment, conventional treatment with ozone/biofiltration, and microfiltration processes as the pretreatment step to membrane-based desalting; and

2. Evaluate full-scale conventional treatment as the pretreatment step to membrane-based desalting.

3. Model the cost savings associated with a 100 million-gallon-per-day (mgd) desalting plant using conventional treatment (both with and without ozone and biologically active filters) versus microfiltration as the pretreatment step

Project Approach

RO membranes were tested following pilot-scale conventional treatment, conventional treatment with ozone/biofiltration, and microfiltration. The RO membranes were operated on each pretreatment to determine specific flux, salt rejection, and fouling potential. In addition to pilot-scale testing, five different RO membranes were evaluated using full-scale conventional treatment with aluminum sulfate or ferric chloride coagulation. The RO membranes were operated to determine membrane productivity (flux), salt rejection, and cleaning frequency. Data collected during these tests included flows, pressure, conductivity, and water quality.

Project Outcomes

Pilot-Scale Testing

Microfiltration produced water containing lower particle counts, turbidity, and silt density index (SDI) than either conventional treatment or conventional treatment with ozone/biofiltration. However, all three pretreatments produced waters with median turbidity less than 0.1 NTU and median SDI less than or equal to 3, which were lower than the RO membrane manufacturer's recommendations (less than 1

NTU and less than 5 SDI, respectively). Little variation between influent and effluent solute concentrations was observed for each of the three pretreatment processes.

Pretreatment using conventional treatment showed the poorest RO performance in terms of maintaining stable flux over time, followed by conventional treatment with ozone/biofiltration, and finally microfiltration. The average flux for the RO membranes using conventional treatment, conventional treatment with ozone/biofiltration, and MF was 0.28, 0.35, and 0.23 gfd/psi, respectively. The lower specific flux for the microfiltration pretreatment phase was due to operation with different RO elements and not indicative of pretreatment performance. Cleaning frequencies for the RO membranes were once per month and once every two months for conventional treatment and conventional treatment with ozone/biofiltration, respectively. The RO membranes only required chemical cleaning after three months of operation when using MF pretreatment due to purposely introducing a foulant into the system. Salt rejection of the membranes for all three pretreatment technologies ranged from 97 to 99 percent

Full-Scale Testing

Testing with Aluminum Sulfate

A total of five different RO membranes were tested at the F.E. Weymouth Filtration and Robert F. Skinner Filtration plants using alum coagulation and chloramines. Repeated testing with multiple RO elements revealed rapid deterioration in specific flux (up to 60 percent over 100 hrs of operation), as well as progressive reductions in salt rejection (typically 3 to 4 percent over 500 hrs of operation). Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis of the fouled membranes revealed that the foulant was primary aluminum hydroxide and aluminum silicate materials.

Testing with Ferric Chloride

In contrast to the RO data using alum coagulation that showed declining specific membrane flux, the specific flux data when using ferric chloride and chloramines increased over time for all membranes. However, salt rejection for each membrane decreased significantly during testing. These data suggested that the RO membranes were physically degrading over time. SEM and EDS data showed that the

foulant was inorganic in nature and comprised mainly of aluminum, iron, and silica. The RO membranes may have been degraded by residual iron catalyzing a chlorine-amide reaction on the membrane surface, despite the chlorine being present as chloramines.

Economic Evaluation

Preliminary cost estimates for retrofitting a 300-mgd conventional filtration plant using split-flow treatment showed that utilizing the existing conventional treatment plant as the pretreatment step to a 100-mgd RO system was the lowest cost option ($0.39/1000 gal of finished water). While providing excellent pretreatment for the RO system, MF showed at least a 10 percent higher cost to retrofit an existing facility using split-flow treatment with reverse osmosis ($0.44/1000 gal) due to the need to install additional pretreatment facilities. Using this criterion, the project goal of reducing the overall treatment costs by 10 percent was met using conventional treatment as the pretreatment step to RO. The addition of ozone and biological filtration lowered the RO capital costs, but increased the overall treatment costs to $0.52/1000 gal of finished water, again due to the need to install new pretreatment equipment. While using existing conventional treatment plants can potentially save millions of dollars in capital expenditures, the RO costs associated with using conventional treatment are significantly higher than with using either microfiltration or conventional treatment with ozone/biofiltration. Additionally, high membrane fouling rates associated with using conventional treatment may reduce this option's feasibility.

Conclusions and Recommendations

Pilot-Scale Results

Despite each pretreatment tested (conventional treatment with and without ozone biofiltration and microfiltration) providing high-quality effluent water, dramatic differences in RO performance was observed. The conventional treatment phase required chemical cleaning three times within the three-month test period due to organic and biological fouling that resulted in a loss of specific flux. However, the performance of conventional treatment was improved through the addition of pre-ozonation and operating the filters biologically active. Despite being operated at higher flux, conventional treatment with ozone/biofiltration slowed the RO membrane rate of fouling by a factor of 2. The improved

performance for biofiltered water may have resulted from the stabilization of the (natural organic matter) NOM through the ozonation/biofiltration process. Microfiltration provided the highest quality water to the RO process and thus resulted in the lowest cleaning frequency.

Full-Scale Results

Testing with full-scale conventional drinking water treatment showed differing results from the pilot-scale testing. Conventional treatment using both aluminum sulfate and ferric chloride coagulation resulted in adverse membrane performance that would hinder full-scale implementation of RO technology. During RO testing using alum coagulation (6 to 8 mg/L), alum residuals (aluminum hydroxide) and colloidal clay materials (aluminum silicates) rapidly accumulated on the membrane surface and caused a loss in flux. However, salt rejection was largely unaffected. In contrast to results obtained using alum, when ferric chloride (4 to 5 mg/L) was used as the primary coagulant, the specific membrane flux increased at the same time the salt rejection decreased. It was theorized that the residual iron in the pretreatment effluent aided in the deacetylation reaction on the membrane surface that resulted in membrane degradation, though the exact reaction pathway was not determined.

Economic Evaluation

The project goal of reducing the overall treatment costs by 10 percent was met using conventional treatment as the pretreatment step to RO. However, high membrane fouling rates associated with using conventional treatment may reduce this option's feasibility. The addition of either ozone and biological filtration or MF lowered the RO capital costs, but increased the overall treatment costs due to the need to install new pretreatment equipment.

ABSTRACT

In order to aid State municipalities in desalination of various water sources, this project was conducted to evaluate if existing conventional treatment plants (with and without ozone/biofiltration) can serve as the pretreatment step to Colorado River water desalination. Reverse osmosis (RO) membranes were operating using various pretreatment technologies (conventional treatment, conventional treatment with ozone/biofiltration, and microfiltration), as well as different coagulants during the conventional treatment process (aluminum sulfate and ferric chloride). Experimental data were used to estimate the cost associated with designing a 300-mgd split-flow, desalting facility. Results from this project showed that pretreatment using conventional treatment achieved the poorest RO performance in terms of maintaining stable flux over time, followed by conventional treatment with ozone/biofiltration, and finally microfiltration. Aluminum sulfate (6 to 8 mg/L) coagulation resulted in rapid loss of flux due to the accumulation of aluminum hydroxide and aluminum silicate materials on the membrane surface. Ferric chloride (4 to 5 mg/L) coagulant residuals aided in the chemical degradation of the membrane surface that resulted in an increase in flux and decrease in salt rejection. The project goal of reducing the overall treatment costs by 10 percent was met using conventional treatment as the pretreatment step to RO. However, high membrane fouling rates associated with using conventional treatment may reduce this option's feasibility. The addition of either ozone and biological filtration or microfiltration lowered the RO capital costs, but increased the overall treatment costs due to the need to install new pretreatment equipment.

INTRODUCTION

Southern California receives approximately sixty percent of its water from northern California, the eastern Sierras, and the Colorado River. While these water supplies are critical to southern California's economy, the practice of importing water, most notably from the Colorado River, has created a salt imbalance problem. Simply stated, approximately 630,000 tons of salt per year accumulates within the southern Californian coastal plain (Metropolitan Water District 1998). Colorado River water contains upwards of 700 milligrams per liter (mg/L) of total dissolved solids (TDS) with potential increases to 750 mg/L of TDS in the near future. This accumulation of salt causes broad, societal damages due to impaired groundwater aquifers and scaling and corrosion of plumbing fixtures, among other things. Recent studies conducted by Metropolitan (1998) have shown that through the use of Colorado River water, approximately $95 million per year in damages are incurred to the public and private sectors for every 100 mg/L of TDS over 500 mg/L—the U.S. Environmental Protection Agency's secondary, non-health standard for TDS. In order to offset these societal costs and provide a reliable supply of safe and aesthetically pleasing water, the Metropolitan Water District of Southern California (Metropolitan) is evaluating new and promising water treatment technologies. A planning goal at Metropolitan is to meet or exceed the 500 mg/L TDS secondary standard. One option to accomplish this goal is through desalination.

Metropolitan owns and operates five large, conventional treatment filtration plants that supply potable water to over 17 million southern Californians. Unfortunately, the conventional approach to water treatment does not include a process for salt removal. Therefore, new technologies will need to be developed and installed to mitigate damages from current water sources, namely Colorado River water. However, prior to any desalination step, the feed water must be conditioned, or pretreated, by removing the suspended solids and biological material. Adequate pretreatment is vital for the long term performance of the desalination technology, whether it is a membrane or distillation-based process.

This project was conducted by Metropolitan to investigate various pretreatment technologies for use with Colorado River water desalination. Pretreatment technologies investigated included conventional treatment (coagulation, flocculation, sedimentation, multi-media filtration); conventional treatment with

ozone disinfection and biofiltration; and microfiltration. This research will assist municipalities to minimize the cost of salinity reduction and may also be applicable to other surface water supplies.

Background

The quality of the feed water supply is the single most important factor to be considered in ensuring the technical and economic viability of a membrane plant (Morin 1994). While the growing consensus of water treatment professionals is towards replacing aging conventional treatment plants with membrane filtration systems (Martinez 1999, Duranceau 2000), one of Metropolitan's research goals is to determine if conventional treatment can serve as the pretreatment to a desalting facility in a cost-effective manner.

Conventional Treatment Processes

Metropolitan has been operating conventional treatment plants using CRW since 1940. Over this time, conventional treatment has been successfully demonstrated to meet the particle filtration needs prior to disinfection. However, conventional treatment does little to reduce the TDS of the water, in fact, the TDS may increase slightly by adding coagulant salts or through pH adjustment. While Metropolitan's treatment plants consistently produce high quality, low turbidity water, Metropolitan's member agencies desire lower TDS water (less than 500 mg/L of TDS) to be delivered year round. Little research has been conducted on the use of conventional treatment plants prior to salinity reduction for surface waters. Existing conventional surface water treatment plants would be ideal locations for salinity removal facilities, where space is available, since staff and treated water pipelines are already present. Since conventional treatment facilities at Metropolitan are already in place, significant savings could be realized by avoiding microfiltration (MF) and ultrafiltration (UF) pretreatment. This alone could reduce overall surface water desalination costs by about 17 percent (Metropolitan 1998).

Many water treatment plants throughout the United States are switching to ozone disinfection. Water treatment plants employing ozone disinfection must also operate their filters biologically to remove assimilable organic carbon, an indicator of biological regrowth that is greatly increased by ozonation (USEPA, 1994). Water treated by conventional treatment with ozone/biofiltration contains lower levels

of natural organic matter (NOM), which contributes to membrane fouling (Carlson and Amy 1998, Volk and LeChevallier 2000). Miltner et al. (1996) showed that ozone/biofiltration removed more dissolved organic carbon (DOC) and biodegradable DOC than conventional treatment alone. This substrate reduction may minimize biofouling on downstream membrane processes. However, biofilters generally have higher levels of viable bacteria leaving the filters, which may exacerbate biological fouling. These issues needed to be investigated before conventional treatment and conventional treatment with ozone/biofiltration can be considered viable pretreatment alternatives. Microfiltration, conventional treatment, and conventional treatment with ozone/biofiltration were evaluated as possible pretreatment options for full-scale use.

Low-Pressure Membranes

Membrane filtration processes such as MF and UF produce a better (i.e., lower) silt density index (SDI) than the conventional treatment process, resulting in less particulate and biological fouling of downstream membrane units (Anselme and Jacobs 1996, Jacangelo and Buckley 1996). Low-pressure membrane processes occupy a smaller footprint, require comparable energy, and are more effective at removing the precursors to biological fouling. Membrane filtration processes also provide superior pathogen removal (e.g., *Giardia* and *Cryptosporidium*) than multi-media processes (Jacangelo and Buckley 1996, Freeman et al. 2000). Lastly, MF and UF processes are more environmentally friendly in that they use little or no chemical coagulants and generate less residuals requiring ultimate disposal.

Up until recently, low-pressure membrane filtration suffered from poor cost competitiveness compared to conventional treatment. However, while conventional treatment technologies have changed little over the past 60 years, MF and UF technologies are undergoing dramatic improvement, resulting in lower capital costs. It is expected that, over the next few years, low-pressure membrane filtration will become more standardized, much like reverse osmosis (RO) membranes did over the previous 20 years, and become less expensive compared to conventional treatment (Duranceau 2000). Based on these qualities, MF was chosen as the benchmark technology to compare the conventional treatment processes against.

Salinity Reduction Step

For the purposes of this study, RO was selected as the primary desalting technology. Reverse osmosis is a pressure-driven membrane separation process that removes ions, salts, and other dissolved solids and non-volatile organics. The unique properties of RO membranes to reject inorganic species while passing relatively pure water has lead to the widespread use of membrane processes to treat various water sources. However, as excessive water is passed through the membrane (i.e., the water recovery is too high), increased fouling may occur in the form of particulate fouling, biological fouling, or scaling.

Project Objectives

The technical objectives of this task were:

1. Evaluate pilot-scale conventional treatment, conventional treatment with ozone/biofiltration, and microfiltration processes as the pretreatment step to membrane-based desalting; and

2. Evaluate full-scale conventional treatment as the pretreatment step to membrane-based desalting of Colorado River water.

The economic objective of this task was:

3. Model the cost savings associated with a 100 mgd desalting plant using conventional treatment (both with and without ozone and biologically active filters) versus microfiltration as the pretreatment step.

PROJECT APPROACH

This section details the experimental methods used for the three project tasks: (1) evaluate pretreatment processes prior to RO treatment; (2) evaluate full-scale conventional treatment as the pretreatment step to membrane-based desalting of Colorado River water; and (3) model the cost savings associated with a 100 mgd desalting plant using conventional treatment (both with and without ozone and biologically active filters) versus microfiltration as the pretreatment step.

Source Water

This study was originally designed for 100 percent CRW; however, the majority of the time, the feed water consisted of a 75/25 percent blend of CRW and California State Project water (SPW). Blends higher in SPW had significantly less influent TDS and sulfate but slightly more iron, aluminum, and silica. Although the study was mainly designed for 100 percent CRW, information on the effects of RO desalination using blended waters provided valuable information on operational parameters, limitations, and fouling tendencies.

Pilot-Scale Test Equipment

Pilot-Scale Conventional Treatment Plant.

The conventional treatment consisted of a 60-gallon-per-minute (gpm) package plant (Aqua-4™ series, type LC, model Q-60; Smith and Loveless, Inc., Lanexa, Kans.). The plant consisted of a static mixer, flocculation and sedimentation basins, and dual-media filtration using anthracite coal and sand. Sodium hypochlorite was fed at 3.0 mg/L as NaOCL at the head of the plant, followed by 2.0 mg/L ferric chloride and 0.5 mg/L cationic polymer (polydimethyldiallylammonium chloride [polyDADMAC], Agefloc WT-20, CPS Chemical Co., Inc., Old Bridge, NJ). The package plant was typically operated at a filtrate flow rate of 35 to 40 gpm. After the filtration step, a chloramine residual of 2.0 to 2.5 mg/L was maintained at a chlorine-to-ammonia ratio of 3:1 (w/w). Chloramines have been demonstrated to effectively control biological fouling of downstream membrane processes (Lozier 1999).

Pilot-Scale Conventional Treatment Plant with Ozone and Biological Filters.

The 60-gpm pilot plant was operated with 0.8 to1.2 mg/L ozone dosed prior to the static mixer, and no chlorine was added prior to filtration to allow the filter to ripen biologically. Ozone was supplied by an ozone generator (model GTC-2A®; Griffin Technics, Inc., Lodi, N.J.) using air or oxygen feed. After the biofilters, a chloramine residual of 2.0–2.5 mg/L was maintained at a chlorine-to-ammonia ratio of 3:1 (w/w). The same coagulants and dosages were used as had been used in the conventional treatment phase.

The treatment plant filter was backwashed based on the following criteria, which ever occurred first: 0.1 NTU filter effluent, 3 ft of filter headloss, or 24 hrs of filter run length. Continuous monitoring data for flow, headloss, particle counts, and turbidity for both influent and effluent streams were recorded. Turbidity measurements were taken by a Hach 1720C Turbidimeter (Hach Company, Loveland, CO). Particle count data of the plant effluent were recorded by an IBR Online Particle Monitoring System (Inter Basic Resources, Inc., Grand Lakes, Mich.). Headloss and flow measurements were taken by Rosemount Model #1151 differential pressure gage (La Habra, CA) and Signet Model # MK 585-1 flow meter (Azusa, CA), respectively. pH and free chlorine (measured with on-line probes) of the plant effluent were also monitored continuously.

Microfiltration Unit

Pretreatment to the RO unit was also provided by a 22 gpm microfiltration unit (Model 3M10C, U.S. Filter/Memcor, Timonium, Maryland). The MF unit contained three parallel polypropylene, hollow-fiber membrane modules (0.2 μm nominal pore size; 14.9 m^2 of outside surface area per module) that filter water in an outside-in direction and was operated in dead-end mode. The net driving pressure ranged from 6 to 10 psi yielding a filtrate flow rate of 20 gpm at a flux rate of 60 (gal/ft^2/day) gfd. Air scour backwashing was programmed for every 22 min. A 2.0 to 2.5 mg/L chloramine residual was maintained in the MF feed using sodium hypochlorite and ammonium sulfate (3:1 w/w chlorine-to-ammonia ratio). A chlorine analyzer (Hach Company CL-17 chlorine analyzer, Loveland, Colo.) was connected to the MF unit's programmable logic circuit such that the MF unit would shutdown when the influent free chlorine residual exceeded 0.5 mg/L; thereby, preventing free chlorine from coming in contact with the MF membranes. Turbidity data for the microfiltration unit were taken in batch samples using a Hach 2100N Turbidimeter (Hach Company, Loveland, Colo.). Effluent particle count data (IBR Online Particle Monitoring System, Inter Basic Resources, Inc., Grand Lakes, Mich.) were taken directly after the filtration step. All particle count data were collected once per minute. SDI data were taken just prior to the RO influent (approximately 50 ft away).

The microfiltration unit was cleaned prior to the start of this study. The clean-in-place procedure was conducted according to the manufacturer's specifications. The acid cleaning cycle was followed by a

caustic cleaning cycle. Each cleaning cycle took approximately 2 hrs (15-20 minutes initial recirculation shell, followed by chemical addition with 30 min, 45 min, and 45 min recirculation cycles). The cleaning solution was then drained, and the unit was backwashed three times with raw water. No further cleanings were required during this study phase.

Cleaning solutions were mixed with 40ºC RO permeate water. The acidic solution consisted of ten pounds of citric acid at pH 2.0 to 3.0. The caustic solution used 4.2 L of Memclean (U.S. Filter/Memcor, Timonium, Maryland) and 1.7 L of 35 percent hydrogen peroxide. The pH was typically 12.0 to 12.5.

Three-Element Membrane Test Unit

A pilot-scale RO unit (Nimbus™ Model 6000, San Diego, Calif.) was used to evaluate the pretreatment efficiency of conventional treatment with and without ozone and biologically active filters. The RO unit housed three membranes (FilmTec Enhanced LE; Dow Liquid Separations, Minneapolis, Minn.) in a 2:1 configuration. Antiscalant (1.6 mg/L Permatreat 191; Permacare, Fontana, Calif.) was fed just prior to the RO influent. Because the unit operated at low recoveries (less than 20 percent), no pH adjustment was required. This system was used solely to evaluate the organic, biological, and/or colloidal fouling potential of conventionally treated water.

24-Element Membrane Test Unit

A three-array RO unit (Nimbus™ Model PSMWD-1, San Diego, Calif.) was pilot tested during the microfiltration evaluation phase of this project. The first two arrays used 4-in. diameter pressure vessels with three 4-in. x 40-in. spiral-wound thin-film composite polyamide membrane elements (Koch Fluid Systems TFC-4821ULP, San Diego, Calif.) per vessel. The third array consisted of two 2 ½-in. pressure vessels in parallel. Each 2 ½-in. pressure vessel housed three 2 ½-in. x 40-in. spiral-wound thin-film composite polyamide membrane elements (Koch Fluid Systems TFC-2540-ULP, San Diego, Calif.). The RO unit was operated between 85 and 90 percent recovery rates (i.e., for 90 percent water recovery, the permeate flow was 16 gpm and concentrate flow was 2.0 gpm at 98 percent salt rejection) for the duration of the project. Antiscalant (1.6 mg/L Permacare, Permatreat 191, Fontana,

Calif.) and sulfuric acid (15 to 27 mg/L) were added prior to the RO influent to minimize scaling. The feed to the RO unit was approximately pH 7.0.

Prior to the start of testing, the RO membranes were cleaned using an acidic solution (10,000 mg/L citric acid at pH 2.0 to 2.5) followed by a caustic solution (10,000 mg/L each of EDTA, sodium tripoly-phosphate, and trisodium phosphate at pH 10.0 to 11.0). Additionally, the RO membranes were cleaned when either the normalized flux decreased 15 percent, the differential array pressure reached 30 psi, or a significant increase in salt passage was observed. The cleaning involved isolating each array and recirculating the cleaning solution at 4 to 5 gpm for 20 to 30 min. The membranes were then allowed to soak in the solution for 30 min, followed by an 8 to 9 gpm high flow for 20 min. Finally, permeate water was flushed through the system to return the pH to normal.

Full-Scale Test Equipment

Full-Scale Filtration Plants.

F. E. Weymouth Filtration Plant. The F. E. Weymouth Filtration Plant, located in La Verne, California, is a 520-million-gallon-per-day (mgd) design capacity surface water treatment facility. The Weymouth plant consists of two rapid mix influent channels, eight flocculation basins, eight sedimentation basins, 48 filters and a 50 million-gallon finished water reservoir. Chemical feeds include alum (3 to 5 mg/L), cationic copolymer (1.5 to 3.0 mg/L polyDADMAC) and chlorine (2.0 to 3.0 mg/L as NaOCL).

The filtration process is a constant rate, rising headloss process. A constant water depth is maintained over the filter by gradually opening the filter effluent valves (30 to 60 percent) as headloss across the filter increases. While the design filtration rate for all 48 filters was 4.0 gpm/ft^2, the average historical filtration rate was only 3.0 gpm/ft^2. The filter backwash was initiated when any of the three set point parameters were reached: maximum head loss (6.0 ft), filter effluent turbidity (0.2 NTU), or maximum filter run time (48 hr).

Robert F. Skinner Filtration Plant. The 520-mgd Robert F. Skinner Filtration Plant in Winchester, California was utilized to study the performance of RO membranes, using either ferric chloride or aluminum sulfate (alum) as the primary coagulants. Alum was dosed at 6 to 8 mg/L (as $Al_2[SO_4]_3$) with 1.0 to 1.5 mg/L of cationic polymer (polyDADMAC). Ferric was dosed at 4 to 5 mg/L (as $FeCl_3$) with 1.5 to 2.0 mg/L of cationic polymer (polyDADMAC). The study utilized the filtration plant's direct-filtration modules with tri-media filters (anthracite, garnet, and ilmenite sand). A 2.5 to 3.5 mg/L free chlorine residual was maintained in the filter gallery, the sampling location for this study, and was converted to chloramines through ammonium sulfate addition (3:1 chlorine to ammonia w/w ratio).

The tri-media filters were backwashed based on the following criteria: (1) effluent turbidity levels exceeded 0.2 NTU; (2) or headloss accumulation reached a maximum of 6 ft. For direct filtration, the design filtration rate was 7.4 gpm/ft^2. These filtration rates were based on one of the eighteen filters per module being out of service at any time. Filtration rates based on hydraulic capacity were somewhat higher. It should be noted that filtration rates for the filters were typically maintained at approximately 6 gpm/ft^2. This filtration rate generally provided the greatest unit filter production. Minimum filtration rates were generally maintained at no less than 4 gpm/ft^2. The use of low filtration rates was avoided to prevent surface clogging, rapid headloss accumulation, and decreased unit filter production. To maintain these filtration rates, the number of filters and/or modules in service were varied to attain the desired filtration rate.

Three-Element Membrane Screening Unit

A pilot-scale unit with three parallel pressure vessels was used to evaluate RO membrane performance on conventionally treated water using alum and ferric coagulants. Reverse osmosis membranes tested included: Hydranautics LFC1, ESPA1, and ESPA3, Hydranautics, Oceanside, Calif.; TFC-ULP®, Koch Fluid Systems, San Diego, Calif.; and FilmTec Enhanced LE, Dow Separation Processes, Minneapolis, Minn.. Antiscalant (1.6 mg/L Permatreat 191; Permacare, Fontana, Calif.) was used. Because the unit operated at low recoveries (<10 percent), no pH adjustment was required. This system was used solely to evaluate the organic, biological, and/or colloidal fouling potential of conventionally treated water.

Analytical Methods

The water quality data of the pretreatment and RO processes were collected in the form of hardness, alkalinity, TDS, major cations and anions, trace metals, particle count, turbidity, temperature, pH, and heterotrophic plate count (HPC) bacteria . For a complete list of analytical methods see Appendix A. All sampling was conducted by Metropolitan's staff. Inorganic and microbial analyses were analyzed at Metropolitan's Water Quality Laboratory in La Verne, Calif.

Membrane Autopsy

Upon completion of each pretreatment evaluation phase, the lead RO element was autopsied by Metropolitan personnel. Swatches of membrane material were collected and sent to independent laboratories for microscopic analysis. The following analyses were conducted:

>Scanning Electron Microscopy (SEM) was conducted by the Scripps Oceanographic Institute in La Jolla, Calif. using a Cambridge Instruments Model 360 (Leo Electron Microscopy, Thornwood New York). Membrane samples were prepared for top surface views by cutting a small piece of membrane and then attaching it to an aluminum mount with double-stick tape. Cross-sections were prepared by fracturing a small strip of the membrane while in a liquid nitrogen bath; this was also attached to an aluminum mount. The mounted sample was sputter-coated with a 30 nm layer of gold and palladium.

>Energy Dispersive Spectroscopy (EDS) was conducted in concert with the SEM by the Scripps Oceanographic Institute (Oxford Instruments Model QX2000, Concord Mass.). The membrane sample for EDS analysis was attached to a graphite mount with graphite tape; there was no coating on the sample. This technique was used because graphite is not detected by EDS and does not interfere with atoms being measured in the sample.

Scanning electron microscopy provides a magnified visual picture of the membrane surface. Energy dispersion spectroscopy analysis provides an elemental analysis of elements with atomic numbers greater than 12 (magnesium). Therefore, EDS analysis does not detect the presence of carbon,

nitrogen, or oxygen (atomic numbers 6, 7, and 8, respectively), which are the primary constituents of organic or biological foulants. However, SEM analysis may identify organic and biological fouling through visual identification of bacteria and the physical morphology of the membrane foulant. Used together, SEM and EDS analyses are used to judge the degree and composition of foulant materials on the membrane surface.

Calculated Values

In order to assess the performance of the pretreatment and salinity reduction steps, several key values were calculated based on raw process data. These calculated values include SDI for the pretreatment step, and specific normalized flux and salt rejection for the RO processes (see Appendix B).

PROJECT OUTCOMES

Figure 1 provides a schedule of the pilot- and full-scale testing conducted during this project. A total of five RO membranes were tested during this project, including four ultra-low-pressure polyamide membranes and one chlorine tolerant non-polyamide membrane (see Table 1). Table 2 provides a brief summary of experimental conditions used throughout the pilot- and full-scale testing.

Pilot-Scale Testing

Pretreatment Performance

Table 3 provides a summary of the pilot-scale pretreatment performance. No major problems were observed during the operation of the conventional pilot-plant both with and without ozone/biofiltration. During conventional treatment using 75 percent CRW and 25 percent SPW, the average filter run length was 8.9 hrs at a hydraulic loading of 3.1 gpm/ft^2 (short run lengths were due to rapid increase in headloss). In late February 2000, the feed water to the treatment plant was changed to a 1:1 blend of CRW and SPW due to changes in Metropolitan's distribution system. The treatment plant under these conditions had an average run length of 20.8 hrs at a hydraulic loading rate of 2.9 gpm/ft^2. During the conventional treatment with ozone and biofiltration phase using a 3:1 blend of CRW and SPW, the average filter run length was 13.6 hrs at a hydraulic loading rate of 3.1 gpm/ft^2. Conventional treatment

with ozone/biofiltration was operated both with and without chloramine addition to the biofilter effluent. However, no appreciable change in operational data were observed whether chloramines were added or not.

Figures 2 and 3 show the median influent particle counts and turbidity data, respectively, for each of the pretreatment phases. Influent turbidity and particle count data were taken at the head of the pretreatment processes. The box-and-whisker plots show minimum, 25th percentile, median, 75th percentile, and maximum values. Median influent turbidities ranged from 2.3 NTU for the microfiltration phase to 0.54 NTU for ozone/biofiltration. It should be noted that both conventional treatment and conventional treatment with ozone/biofiltration phases used a 75/25 blend of CRW/SPW, while the microfiltration phase used a 60/40 CRW/SPW blend.

Previous researchers have shown that both raw SPW and raw CRW contain similar levels of assimilable organic carbon (AOC) (83 μg acetate-C median AOC and 94 μg acetate-C median AOC for SPW and CRW, respectively) (Huck et al. *In Press*), as measured by Standard Method 9217 B (APHA, AWWA, and WEF 1998). While the percent removal of AOC across the biofilter was greater for SPW than CRW, suggesting differences in the organic nature of the waters (Hacker et al. 1994, Huck et al. *In Press*), the ozone/biofiltration process has a far greater influence on AOC than water type in this case. Therefore, the change in water quality between test phases may not have influenced the biofouling potential of the raw water.

Figures 4,5, and 6 show pretreatment effluent particle count, turbidity, and SDI data, respectively. Microfiltration produced water containing lower particle counts, turbidity, and SDI than either conventional treatment or conventional treatment with ozone/biofiltration. However, all three pretreatments produced waters with median turbidity less than 0.1 NTU and median SDI less than or equal to 3.1, which were lower than the RO membrane manufacturer's recommendations (less than 1 NTU and less than 5 SDI, respectively).

Microfiltered water demonstrated a median particle count of 1.8 particles/mL (range, 0.02 to 510 particles/mL) and median turbidity of 0.05 NTU (range, 0.03 to 0.5) [see Figure 4 and Figure 5]. The microfiltration turbidity data showed a larger interquartile range than both conventionally treated

waters. This difference may be attributed to the turbidity data being collected using a batch turbidimeter rather than an on-line turbidimeter. The IBR particle counter used during this study had a 2 μm-particle detection limit. Therefore, any particles detected in the MF effluent may be due to microfiber breakage, air bubbles in the line, or instrument error.

The conventional treatment plant produced an effluent with a daily median particle density of 14.3 particles/mL (range, 0.6 to 2,000 particles/mL) and turbidity of 0.1 NTU (range, 0.05 to 0.8 NTU). Turbidity for conventional treatment with ozone/biofiltration was comparable to that obtained for conventional treatment. Conventionally treated water showed a slightly higher median SDI than ozonated/biofiltered water (3.1 versus 2.3, respectively) [see Figure 6]. The SDI for microfiltered water was significantly less than either conventionally treated water (range, 0.5 to 1.5, with a median value of 0.8).

Water quality data for each pretreatment process are shown in Table 4. As expected, little variation between influent and effluent solute concentrations were observed for each of the three pretreatment processes. Changes in individual solutes between pretreatment phases were attributed to changes in influent water quality and are not indicative of pretreatment performance.

Reverse Osmosis Performance

Testing using RO membranes consisted of three conventional treatment runs, two conventional treatment with ozone/biofiltration runs, and one microfiltration run (see Table 5). A summary of the RO performance for each pretreatment type is shown in Table 6. Each of the aforementioned RO runs were terminated due to membrane fouling. Pretreatment using conventional treatment showed the poorest RO performance in terms of maintaining stable flux over time, followed by conventional treatment and ozone biofiltration, and finally microfiltration (see Figures 7, 8, and 9). This was despite the conventional treatment phase being operated at 36 percent lower actual membrane flux than either conventional treatment with ozone/biofiltration or microfiltration. Salt rejection of the membranes for all three pretreatments was generally excellent at 97 to 99 percent (see Figures 10, 11, and 12).

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During conventional treatment, the RO unit was chemically cleaned three times due to either a decline in specific flux or an increase in differential pressure (see Figure 7 and Figure 13). Membrane cleanings were conducted after 636 hrs, 1168 hrs, and 1785 hrs of operation. These cleaning intervals are consistent with another membrane study being conducted simultaneously using the same feed water (Gabelich et al. in press). Upon chemical cleaning using both acidic and caustic cleaning agents, the specific flux recovered to the initial starting point. Upon autopsy of the lead RO element, the membrane surface was coated with a gelatinous reddish-brown material. No inorganic materials were detected on the membrane surface (see Table 7). This finding was consistent for all three conventionally treated RO runs and suggests that either organic or biological fouling of the membranes was occurring. For a representative SEM micrograph, which provides a visual picture of the membrane surface, see Figure 14.

The RO unit using conventional treatment with pre-ozonation and biologically active filters with and without chloramines showed an improvement in RO performance over pretreatment with conventional treatment alone. This was despite the RO membranes under ozone/biofiltration (without chloramine addition) pretreatment being operated initially at over 75 percent higher operating flux than during conventional treatment (21 gfd versus 12 gfd, respectively) (see Table 5)—which typically results in higher rates of colloidal and biological fouling. Given the high initial operating flux, the specific flux showed a steady decline from approximately 0.43 gfd/psi to approximately 0.29 gfd/psi, a reduction of 33 percent over 1,618 hrs of operation (see Figure 8).

In order to decrease the fouling potential caused by the excessive flux rate, the operating flux for the second conventional treatment and ozone/biofiltration was reduced by 24 percent to 16 gfd. However, due to operational constraints of another parallel study, the practice of feeding chloramines to the biofilter effluent was discontinued. Despite the absence of chloramines, the fouling rate significantly declined, which resulted in only a 15 percent reduction in specific flux over 2,111 hrs of operation (see Figure 8). The differential pressure across the RO elements increased significantly, especially during the second ozone/biofiltration run (see Figure 15)—an indication of particulate and/or biological fouling. It should be noted that for surface water applications, a typical RO operating flux would be 15 gfd. Therefore, even at higher than design flux rates (16 gfd), pretreatment with conventional treatment with

ozone/biofiltration resulted in three-fold decrease in cleaning frequency when compared to pretreatment with conventional treatment at a much lower operating flux (12 gfd). Additionally, operating with chloramines has been shown to decrease the membrane cleaning frequency in other studies (Knoell et al. 1999), which may further improve the ozone/biofiltration process.

The RO specific flux values during the microfiltration phase (see Figure 9) ranged from 0.18 to 0.25 gfd/psi for the duration of the run. A significant decline in specific flux was observed at approximately 1,920 hrs of operation due to the introduction of a known foulant into the MF feed as part of another independent study and are not indicative of normal membrane fouling from a microfiltered source water. No significant change in differential pressure was observed during the entire MF pretreatment run (see Figure 16). Microscopic analysis of the membrane surface revealed significant aluminum hydroxide deposits on the membrane surface; however, these foulants were purposely introduced into the MF feed (see Table 7 and Figure 14). No evidence of biofouling was found during the microfiltration pretreatment phase of this project.

Table 8 shows a comparison of the salinity removal for each of the three pretreatment options. Data are presented as percent rejection. During both conventional treatment pretreatment phases, the RO membranes removed 98 percent of the TDS from solution, as measured by gravimetric analysis, with the microfiltration phase removing only 93 percent of TDS. It should be noted that the microfiltration phases were conducted using different RO membranes (Koch Fluid Systems ULP-TFC®) than the other two pretreatment phases (FilmTec Enhanced LE). Additionally, the microfiltration phase membranes were operated for up to 1.5 years using conventionally treated effluent water with ferric chloride coagulation that may have impaired the membrane performance (see discussion in Full-Scale Results). However, differences in the two membrane types used during this phase of the project should not have effected the evaluation of pretreatment on membrane performance. It should be noted that due to non-detectable level for iron in the permeate stream, the percent rejections for iron was not calculated.

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The Effect of Natural Organic Matter and Bacteria on Reverse Osmosis Performance

During this study, biofouling and/or organic fouling caused significant flux loss, most notably during conventional treatment. This section describes the factors that may have contributed to conventional treatment's greater biofouling potential compared to microfiltration. Two of the key differences between microfiltration, conventional treatment, and conventional treatment using ozone and biologically active filters were bacterial loading onto the downstream RO membranes and the composition of the NOM, a food source for the bacteria. Both of these factors may have contributed to the differing RO membrane performances seen using each pretreatment.

Table 9 shows the bacteriological and NOM water quality results taken during this study. In terms of HPC bacteria loading onto the RO membranes, microfiltration provided the lowest plate counts (median 4 cfu/mL). The lower HPC bacteria levels in the microfiltered effluent are due to the 0.2 µm nominal pore size that excludes most bacteria from the effluent stream. As expected, the MF unit had little effect on either the total organic carbon (TOC) or specific ultraviolet absorbance (SUVA). With minimal flux loss and sparse foulants present on the membrane surface after autopsy, it was theorized that despite a food source (NOM) being present, the low bacteria loading coupled with chloramines prevented rapid colonization on the membrane surface.

In contrast to microfiltration, conventional treatment, in addition to having minimal effect on TOC/DOC and SUVA, allowed HPC bacteria to leave the filter media (37 cfu/mL). Therefore, both a food source and bacteria were present in solution. Additionally, the TOC present in the conventionally treated effluent may have been utilized by the bacteria as a growth substrate. Alternatively, the TOC may be adsorbing onto the membrane surface after the extracellular polymeric substances (EPS) layer was formed. In the case of conventional treatment, a suitable environment for bacteriological growth was achieved despite the addition of 2.0 to 2.5 mg/L chloramines.

Effluent from the biofilter showed the highest HPC bacteria levels (11,500 cfu/mL in the biofilter effluent without chloramination and 463 cfu/mL with chloramination) of the three pretreatment processes tested. In addition, conventional treatment with ozone/biofiltration showed an overall reduction in TOC (15 percent) and SUVA (26 percent), which indicated a change not only in the amount of TOC, but

composition as well. Biofiltration has been shown to effectively reduce biodegradable dissolved organic carbon (BDOC) and assimilable organic carbon (AOC) [both not measured as part of this study] (Coffey et al. 1995; Carlson and Amy 1998). The BDOC content represents the fraction of DOC that can be assimilated and mineralized by heterotrophic microorganisms. AOC refers to the fraction of TOC that can be used by bacteria for growth (Volk and LeChevallier 2000). The biostability of ozonated and biologically filtered water has been studied for more than twenty years (Urfer et al. 1997). Previous studies using biofiltration on CRW (Coffey et al.1995) have shown that greater than 100 µg/L AOC remaining in the biofiltered effluent was a causative factor in regrowth downstream of the biofilter (Volk and LeChevallier 2000).

Testing using ozone/biofiltration at 16 gfd for almost three months showed minimal decline in RO performance. However, a visible reddish-brown film was present on the membrane surface, suggesting that biofouling had started. So while bacteria, both viable and nonviable, were present in the RO feed in high numbers, favorable environmental conditions for biofilm production were suppressed, but not eliminated. The biostability of the RO feed prevented the colonization and growth of bacteria on the membrane surface for over two months.

Full-Scale Testing

Testing on the pilot-scale provided a valuable screening tool to determine the efficacy of various pretreatment processes prior to RO treatment. At the pilot-scale, operational conditions may be tailored such that the optimal conditions for successful RO treatment may be established. However, these operational conditions (e.g., at specified coagulant dose and type) may not be obtainable on the full-scale due to inflexible operational limitations. For example, pilot-scale data for conventional treatment was obtained using only a 2.0 to 2.5 mg/L of ferric chloride and 0.5 mg/L cationic polymer. During full-scale operation at two of the five Metropolitan owned drinking water filtration plants that comply with all Safe Water Drinking Act regulations, the coagulant and polymer are maintained at much higher doses (4.0 to 5.0 mg/L and 1.5 to 3.0 mg/L of ferric chloride and polymer, respectively). Additionally, aluminum sulfate (alum) is used at the remaining three Metropolitan drinking water plants. Therefore, in order to determine the potential RO performance given full-scale conditions, a three-

element RO unit was operated on the effluent of two of Metropolitan's drinking water treatment plants (F. E. Weymouth, and Robert F. Skinner filtration plants).

F. E. Weymouth Filtration Plant Results

Testing at the F. E. Weymouth Filtration Plant was conducted using conventionally treated water from the 1.0-million-gallon storage tank used to backwash the dual-media filters. Table 10 lists the effluent water quality data for the Weymouth Plant. A total of five RO membranes were tested during this study; see Table 1 for a complete listing of membranes used and their corresponding tracking code.

Table 11 provides a detailed chronology of operation observations over 2,200 hrs of operation. Figure 17 shows the particle count and turbidity data from the effluent of the F. E. Weymouth Filtration Plant during this period of testing. The F. E. Weymouth Filtration Plant provided excellent particulate removal as evidenced by less than 5 median particles/mL (2 μm detection limit) and median turbidities of less than 0.1 NTU. Effluent water quality data was similar to that found during pilot-scale testing with the exception of aluminum (median value 230 μg/L) (see Table 10).

Figure 18 and Figure 19 show the specific membrane flux and salt rejection, respectively, over time for each of the four test membranes. Repeated testing with multiple RO elements revealed rapid deterioration in specific flux (up to 60 percent over 100 hrs of operation), as well as progressive reductions in salt rejection (typically 3 to 4 percent over 500 hrs of operation). While the low-fouling composite RO element (RO3) showed lower reductions in specific flux over conventional ultra-low-pressure RO elements (RO1 and RO2), the low-fouling composite membrane demonstrated similar declines in salt rejection. Element RO4 (a conventional ultra-low-pressure polyamide membrane) showed similar flux and salt rejection behavior as RO1 and RO2. Therefore, the experimental conditions overwhelmed the low fouling advantage of the RO3 membrane.

A visual inspection of the particulate matter collected on the 5 μm prefilter determined that a majority of the deposited material was inorganic in nature, with some diatoms and other unicellular organisms present. SEM and EDS data of the fouled RO membrane surface also concluded that the deposited material was inorganic in nature (see Figure 20 and Table 12). It was concluded that due to the

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frequent filling and draining of the backwash tank, which was the source water to the RO unit, suspended solids and fine particulates were introduced into the RO feed water, hence causing the rapid fouling events. The performance of the RO unit during this test may not have been indicative of pretreatment using full-scale conventional treatment due to the sampling location. In order to rectify this problem, the RO unit was moved to the Robert F. Skinner Filtration Plant.

Robert F. Skinner Filtration Plant Results

The Robert F. Skinner Filtration Plant offered the unique opportunity to conduct RO testing using a full-scale conventional treatment plant operated with both alum (6.0 to 8.0 mg/L) and ferric chloride (4.0 to 5.0 mg/L) coagulants. Table 10 lists the effluent water quality data for the Skinner Plant. Testing for this phase of the project used ultra-low-pressure polyamide membranes (RO1, RO2, and RO4) (see Table 1). The applied feed pressure was the same for each RO element (75 to 85 psi). The RO feed water was taken after the tri-media filters and prior to the clearwell. Filter effluent particle count, turbidity, and SDI data are shown in Figure 21.

Testing with Aluminum Sulfate

Figure 22 shows the specific normalized flux for all three membranes using Robert F. Skinner filter effluent with alum coagulation. After 1,600 hrs of operation, each of the three ultra-low-pressure membranes exhibited steady declines in specific flux (46 percent for RO1, 59 percent for RO2, and 19 percent for RO4). RO1 demonstrated the highest initial specific flux (0.37 gfd/psi), while RO4 demonstrated the lowest percent change in specific flux (19 percent). However, salt rejection for each membrane did not change significantly through the test (see Figure 23); though membrane RO2 under performed compared to the other two membranes (median salt rejection 95 percent compared to 99 percent).

SEM and EDS data show that the foulant was inorganic in nature and comprised mainly of aluminum, phosphorus, and silica, suggesting the presence of aluminum hydroxides and/or aluminum silicate fouling (see Figure 24 and Table 12). Alternatively, the detection of aluminum and phosphorous may have been caused by the excess aluminum from the coagulation process chelating with the phosphonate-

based antiscalant. Multivalent ions have been shown to form precipitates with soluble phosphates (Metcalf and Eddy 1991).

Results from the full-scale testing at the Robert F. Skinner Filtration Plant using alum coagulation support the fouling tendencies observed during full-scale testing at the F. E. Weymouth Filtration Plant. However, while the magnitude of fouling was comparable between the two plants, the rate of fouling at the Skinner plant was 25 percent less.

Testing with Ferric Chloride

Figure 25 shows the specific normalized flux for all three membranes using Robert F. Skinner effluent with ferric chloride coagulation. In contrast to the RO data using alum coagulation that showed declining specific membrane flux, the specific flux data using ferric chloride increased over time for all membranes (61 percent for RO1, 80 percent for RO2, and 34 percent for RO4) (see Figure 25). As during the full-scale alum testing, RO1 demonstrated the highest initial specific flux (0.31 gfd/psi), while RO4 demonstrated the lowest percent change in specific flux (34 percent). However, salt rejection for each membrane decreased significantly during the test (see Figure 26). These data suggest that each of the RO membranes were physically degrading over time. No leaks in any of the RO unit fittings or O-rings were detected and the membrane performance trends were consistent regardless on membrane type. Additionally, RO4 was sent back to the original equipment manufacturer and the increased flux and lowered salt rejection were confirmed at their laboratory.

SEM and EDS data show that the foulant was inorganic in nature and comprised mainly of aluminum, iron, and silica (see Figure 24 and Table 12). Sulfur was consistently detected by the EDS method due to the sulfur content of the polysulfone support layer of the membrane.

Previous researchers (Murphy, 1991a, Murphy 1991b, and Murphy and Moody 1997) have shown that multivalent salts (e.g., iron) accelerate the deacetylation of cellulose acetate membranes in the presence of free chlorine. The proposed reaction pathway was soluble iron catalyzing the reaction between aqueous chlorine and the hydroxyl and ester functional groups on the polymer ring. However, polyamide membranes, which were used during this study, do not have either ester of hydroxyl

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functional groups as part of the aromatic ring structure (see Figure 27). The activation energy for hydrolysis of the amide functional group is much greater than that for esters (Solomons 1990). Additionally, chlorine present during this study was in the form of chloramines, which has been shown to be compatible with polyamide membranes in other applications (Lozier 1999). Therefore, while chlorination of the polyamide membrane surface may be occurring, an alternate reaction pathway should be investigated—possible through attack of the amide bond connecting the membrane monomers.

In order to confirm that the presence of chloramines and ferric chloride coagulation residuals were the cause of the increased membrane flux and reduced salt rejection, the experiment was repeated with the exception that the free chlorine was quenched with sodium bisulfite (Spectrum Chemical, Gardena, Calif.) (1:1 w:w sodium bisulfite to chlorine). A parallel RO unit was operated using chloramines to serve as a control. Free chlorine residuals using the thioacetamide modification were taken daily (Standard Method 4500-Cl F; APHA, AWWA and WEF 1998).

Figure 28 shows the specific flux for the three RO membranes operated without chloramines and the one RO membrane operated with chloramines. While linear regression of the data indicates that all four membranes showed increases in specific flux over 1,200 hrs or operation, the membrane exposed to chloramines (RO2 with NH_2Cl) showed a sharper increase in specific flux than the membranes not exposed to chloramines (RO2, RO3, RO4). It should be noted that due to frequent power interruptions, the RO unit was stopped and started, up to three times a week; hence the data were variable from point to point. All four membranes, whether exposed to chloramines or not, showed equivalent declines in salt rejection over time (see Figure 29). Daily free chlorine residual measurements were negative for both chloramine and quenched chlorine samples; therefore the likelihood of free chlorine coming into contact with the membranes was minimal. Results from these tests indicate that the iron-catalyzed, chlorine-oxidation pathway may not adequately describe why the membranes during full-scale testing with ferric chloride became compromised over time.

Visual inspection of the elements (RO2 without chloramines and RO2 with chloramines) during autopsy showed that the fouling was much more pronounced on the membrane without chloramines. Additionally, samples of the membrane material were eluted with a phosphate buffer, shaken for fifteen

minutes, and then plated with 1 mL on R2A agar to confirm the presence of bacteria. Preliminary results showed high levels of bacteria present on the membrane exposed to chlorine-free water, and significantly less bacteria were present on the membrane exposed to chloramines. Microscopic analyses of two of the fouled membranes are shown in Figure 30. For membrane RO2 without chloramines, the EDS data (Table 13) showed high levels of aluminum, iron, silica, phosphorus, and calcium, suggesting the presence of aluminum silicate fouling. The presence of phosphorus may indicate the presence of the phosphonate-based antiscalant. Inorganic analysis of the membrane RO2 exposed to chloramines revealed the presence of silica and smaller levels of chloride, calcium, and iron were present on the membrane surface. The data indicate that for both membranes showed inorganic fouling, but the membrane exposed to chlorine-free water also showed evidence of biological fouling—most likely due to the absence of chloramines.

Economic Modeling

A hypothetical 300-mgd treatment plant was designed utilizing split-flow treatment where a portion of the plant flow was desalted and then recombined with the main plant flow to produce a 500 mg/L TDS product water. A total of three pretreatment options were evaluated (see Figure 31). The first option used a pre-existing conventional treatment plant to treat approximately 66 percent of the total plant flow and a separate 100-mgd product water MF/RO facility to desalt a side-stream of the total plant influent. The second option studied used a conventional treatment plant to treat the total influent flow with a split-flow stream being desalted by RO. The third option used ozone/biofiltration on the total influent flow followed by RO on only a side-stream of the biofilter effluent. This option was studied due to changing water quality goals that may dictate Metropolitan using ozone on the full-stream of each of its five treatment plants.

The location of the desalting facility was assumed to be at an existing conventional water treatment plant; therefore, the purchase of additional land was not needed. Internal Metropolitan data were used to calculate both capital and operation and maintenance (O&M) costs for the conventional treatment processes. The basic conventional treatment plant was assumed to already be in-place with fully amortized capital. All other processes were assumed to be new, and thus would have capital and

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O&M costs associated with their implementation. The amortization rate and period (6 percent and 20 years, respectively) were chosen based on established finance and planning practices at Metropolitan.

Pretreatment

Cost estimates for all three pretreatment technologies are shown in Table 14. These costs were based on generic cost equations for new 100-mgd conventional treatment (Qasim et al. 1992) and microfiltration (Black and Veatch 1997) plants and should only be used as rough cost estimates for comparative purposes. Note, energy usage for ozone was updated based on internal Metropolitan data to better reflect actual costs. All treatment costs were adjusted to 2000 U.S. dollars.

Microfiltration was used as the pretreatment process that produces the highest quality of water, although similar results could be obtained with certain ultrafiltration processes. The research on microfiltration in the present study indicated rapid fouling of the MF membranes over long periods of use. This concern would need to be addressed to implement a reliable MF system. However, this factor was not considered in the MF cost calculations. The assumption was made that this operational problem could be resolved through focussed development efforts. MF was used at Metropolitan's desert plants and has been shown to operate reliably at filtrate rates somewhat less than those suggested by the manufacturer. The capital and operating costs used for MF were $0.21 per 1000 gal of filtrate and $0.17 per 1000 gal of filtrate, respectively.

The cost of a new MF system ($0.38/1000 gal) and a new conventional treatment system ($0.37/1000 gal) are comparable. Although MF requires higher energy, it has a number of operational advantages, including higher pathogen removal, lower chemical usage, and a smaller footprint. In addition, the development of immersed ultrafiltration membrane (Mourato et al. 1999) and submerged MF membrane (Johnson 1999, Freeman et al. 2000) processes may lower the costs of future MF and UF plants significantly. In this light, construction of a new desalting facility would invariably use MF as the RO pretreatment process because of the higher quality of the microfiltration effluent.

Use of conventional treatment at Metropolitan and many other sites, would be less costly than a process requiring new equipment since the capital facilities already exist and are fully amortized. For this report there was no capital cost associated with conventional treatment. O&M costs were based on internal data. Costs for adding ozone/biofiltration were estimated based on internal calculations made to assess the cost of this technology for two of Metropolitan's treatment plants. Previous studies have shown that the existing anthracite/sand filters are suitable for use as the biological media for treating SPW and CRW (Coffey et al. 1995). The costs include the use of acid and caustic solutions to adjust the pH of CRW to achieve target disinfection and disinfection by-product levels.

Reverse Osmosis Cost Analysis

Metropolitan developed a large-scale, desalting plant model for this project (see Figure 32). It was assumed that split flow treatment was used to achieve 500 mg/L TDS. The model has been incorporated into a Microsoft Excel® Spreadsheet to make the necessary calculations. The RO plant design was based on the concept of small RO "building blocks" of 5.0 mgd each. These blocks were replicated to treat the entire desalted flow. Thus, the RO plant costs would scale linearly, and economy-of-scale savings would only be realized for site work and system-wide controls.

The RO performance parameters and economic assumptions used to determine cost and energy consumption are listed in Table 15. These data were prepared by CH2M HILL (Gainesville, Florida) in conjunction with Metropolitan. Salt rejection, energy consumption, and cleaning requirements were based on experimental data collected during this study. Based on the results of this project, the membrane fouling rates for microfiltration were assumed to be twice per year, while the RO membrane fouling rates for conventional treatment and conventional treatment with ozone/biofiltration were assumed to be 12 times per year and 4 times per year, respectively. Note: the six-month membrane fouling rate for microfiltration was a conservative estimate and may be significantly longer. Given the different RO feed water quality generated by each pretreatment type, the RO system design flux was modified for each pretreatment scenario to minimize fouling. Therefore, for MF pretreatment the design flux was set at 15 gfd, the upper limit for surface water desalting. The design flux for conventionally

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treated and ozonated/biofiltered waters were assumed to be 10 gfd and 12 gfd, respectively; these lower flux rates reflect the higher membrane fouling rates when compared to MF pretreatment.

The influent TDS was assumed to be 750 mg/L. This was chosen because of the agreement made by seven Colorado River basin states that that the salinity below the Parker Dam will be at or below 747 mg/L of TDS (Colorado River Salinity Control Forum 1996). This standard was specified in section 303 of the Clean Water Act. For estimating costs, specific flux was assumed to be the same for all three pretreatment phases (0.32 gfd/psi) despite the MF phase being operated with a different membrane type. This was used to determine the applied feed pressure that would be needed (140 psi) at an average temperature of 64ºF (18ºC).

Table 14 shows the modeling results for all three treatment options. Experimental results from this project indicated that RO membranes foul at least 3 to 6 times more frequently when using conventional filtration for RO pretreatment, compared to using conventional treatment with ozone/biofiltration and microfiltration, respectively. Based on these data, the RO treatment costs using conventional pretreatment were estimated to be about 12 percent higher than using MF pretreatment and 6 percent higher than using conventional treatment with ozone/biofiltration. The higher costs were calculated assuming that the RO membrane operating flux under conventional treatment conditions (10 gfd) was 33 and 17 percent lower than when using either MF (15 gfd) or conventional treatment with ozone/biofiltration (12 gfd), respectively. Lowering the operating flux was done to overcome the higher membrane-fouling rate for the conventionally treated waters when compared to MF pretreatment. However, if the high membrane fouling rates using conventional treatment are not resolved by lowering the operating flux, further increases in energy consumption, chemical usage, and labor may also be expected; thereby resulting in increased RO treatment costs.

Brine Treatment and Disposal

A fixed RO brine disposal cost without brine treatment was assumed for all options. Research in this area was in progress, and should provide solid costs estimates in the near future. For the purposes of this chapter, the RO brine was assumed to be 15 percent of the RO process influent, and disposal consisted of building a 30 mile pipeline from the treatment plant to the ocean. The estimated cost of the

brine line was $20.5 million. This cost did not assume any site-work, purchase of land, environmental clearance, or other contingencies that may increase the cost substantially. To meet water supply goals (300 mgd), additional water would have to be imported to compensate for the lost water associated with the brine disposal. Both the costs of the brine line ($20.5 million) and the make-up water ($5.1 million per year) remained fixed for all pretreatment scenarios.

It should be noted, in the strongest terms, that this level of water loss (approximately 18 mgd) would be unacceptable in the arid Southwest. Additionally, the cost of design and construction of a 3 ft diameter brine line would certainly be substantially higher than the $20.5 million cost cited above due to the environmental impact report process, legal issues associated with gaining either the necessary right-of-way or land, or other cost factors. Brine treatment technologies to reduce the total disposal volume are both expensive and energy intensive, and are beyond the scope of this project.

Total Treatment Plant Cost Analysis

General capital, operations and maintenance (O&M), and total system costs for each of the three filtration processes are shown in Table 17. The total cost to retrofit a treatment plant was strongly influenced by the availability of existing equipment and infrastructure. For example, the capital expense of some Metropolitan treatment plants have been fully amortized. Thus, cost calculations were made assuming only O&M costs for conventional treatment. Conversely, systems such as microfiltration would have to be newly constructed, although some infrastructure (purchase of land, chemical storage, etc.) may be available and may slightly reduce costs.

While the complete RO system cost was the least using microfiltration as the pretreatment step ($0.78/1000 gal [$2.95/m^3] for microfiltration versus $0.89/1000 gal [$3.37/m^3] for conventional treatment), the total treatment cost for this option was 10 percent higher than conventional treatment ($0.44/1000 gal [$1.67/m^3] and $0.39/1000 gal [$1.48/m^3] for microfiltration, and conventional treatment, respectively) (see Table 17). This higher cost was largely associated with the added capital and O&M costs of building a new pretreatment (microfiltration) facility. From an energy usage perspective, conventional treatment followed by RO may be at least 19 percent more energy efficient

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than a split-flow microfiltration/RO system (0.51 kWh/1000 gal of finished water for conventional treatment with split-flow RO and 0.63 kWh/1000 gal of finished water for split-flow MF/RO).

The above costs for finished water included the costs of filtration, desalting, brine disposal, and purchase of additional water to make up for water lost in brine disposal. It should be noted that these costs would be excessive for economic implementation for such a large-scale plant. They represent a minimum four-fold increase in the treatment costs compared to the current treatment cost of a fully depreciated, large-scale conventional treatment plant ($0.09/1000 gal). Thus, the treatment cost would approximately quadruple. However, the negative economic impacts associated with using relatively saline Colorado River water would be mitigated.

Future treatment schemes must be designed to meet stricter water quality regulations. For example, USEPA Disinfectant and Disinfection By-product regulations may require the use of ozone disinfection in place of chlorine disinfection to limit the formation of chlorinated compounds of trihalomethanes and haloacetic acids. Ozone will become an important disinfectant at many plants because it does not generate chlorinated by-products. Therefore, ozone treatment of the full plant influent flow may be required at all five Metropolitan treatment plants to meet future, more stringent regulations. As expected, utilizing ozone on the full treatment flow further increased the total treatment cost (see Table 17). The cost for this treatment scenario would be $0.52/1000 gal ($1.97/m^3), or at least 25 percent more expensive than using either conventional treatment or microfiltration. This cost included increased capital expenditures to retrofit the complete existing plant with ozone and biofiltration. The conventional treatment/RO system also had significantly lower energy consumption at 0.51 kWh/1000 gallons compared to 0.64 kWh/1000 gallons for ozone/biofiltration and split-flow RO treatment.

The economic goal of this project was to reduce the overall cost of desalting Colorado River water by 10 percent. Results from this project show that despite higher RO treatment costs, the savings which are associated with using the existing conventional treatment facilities makes conventional treatment the lowest cost option. While using conventional treatment facilities saved over 10 percent when compared to MF/RO treatment, the high rate of membrane fouling using conventional treatment may reduce this cost savings significantly. One method to improving membrane performance was to retrofit the existing

conventional treatment plant with ozone and biological filtration. However, while meeting multiple water quality objectives, this option was the most expensive and energy intensive.

CONCLUSIONS AND RECOMMENDATIONS

Pilot-Scale Results

Given the relatively low turbidity and low particle-laden source waters available to Metropolitan, each of the three pretreatment technologies tested produced an effluent water quality generally deemed suitable for use with RO (see Table 3). Note: the 0.02 mg/L free chlorine may be an artifact of chloramination and not indicative of the true free chlorine residual. All three pretreatment technologies (microfiltration, conventional treatment, and conventional treatment with ozone/biofiltration) did not significantly alter the effluent concentrations for all inorganic constituents, with the exception of aluminum and iron. However, a major difference in pretreatment performance was the passage of bacteria and TOC.

Microfiltration, having a 0.2 μm nominal pore size, provided the highest bacteria removal of all three pretreatments. Bacteriological data collected after conventional treatment showed a 99 percent removal of HPC bacteria and reduced the coliform bacteria to below the method detection limit. Both microfiltration and conventional treatment had a minimal effect on TOC levels. Conventional treatment with ozone/biofiltration did not reduce HPC counts across the pretreatment process (11,330 cfu/mL in the influent compared to 11,500 cfu/mL in the biofilter effluent prior to chloramination). However, subsequent chloramination of the effluent water reduced the HPC bacteria by 96 percent to 463 cfu/mL. A 15 percent decrease in TOC was observed across the ozone/biofiltration process that may have led to biostabilization of the biofiltered effluent.

Table 6 provides a summary of RO operational data. The conventional treatment phase required chemical cleaning three times within the three-month test period due to organic and biological fouling that resulted in a loss of specific flux. However, the performance of conventional treatment was improved through the addition of pre-ozonation and operating the filters biologically active. Despite being operated at higher flux, conventional treatment with ozone/biofiltration slowed the RO membrane

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rate of fouling by a factor of 2. The improved performance for biofiltered water may have resulted from the stabilization of the NOM through the ozonation/biofiltration process. Microfiltration provided the highest quality water to the RO process and thus resulted in the lowest cleaning frequency.

Full-Scale Results

Testing with full-scale conventional drinking water treatment showed differing results from the pilot-scale testing. Conventional treatment using both aluminum sulfate (alum) and ferric chloride coagulation resulted in adverse membrane performance that would hinder full-scale implementation of RO technology.

While biological fouling was the primary foulant during pilot-scale conventional treatment testing, both with and without ozone/biofiltration, inorganic colloidal fouling and membrane degradation were primary concerns during full-scale testing. During RO testing using alum coagulation (6 to 8 mg/L), alum residuals (aluminum hydroxide) and colloidal clay materials (aluminum silicates) rapidly accumulated on the membrane surface and caused a loss in flux. However, salt rejection was largely unaffected.

In contrast to results obtained using alum, when ferric chloride (4 to 5 mg/L) was used as the primary coagulant, the specific membrane flux increased at the same time the salt rejection decreased. It was theorized that the residual iron in the pretreatment effluent aided in chlorination reaction on the membrane surface that resulted in membrane degradation, though the exact reaction pathway was not determined.

Economic Evaluation

Preliminary cost estimates for retrofitting a 300-mgd conventional filtration plant using split-flow treatment showed that utilizing the existing conventional treatment plant as the pretreatment step to RO was the lowest cost option ($0.39/1000 gal of finished water). While providing excellent pretreatment for the RO system, MF showed at least 10 percent higher cost to retrofit an existing facility using split-flow treatment with reverse osmosis ($0.44/1000 gal) due to the need to install additional pretreatment facilities. By this criteria, the project goal of reducing the overall treatment costs by 10 percent was met

using conventional treatment as the pretreatment step to RO. The addition of ozone and biological filtration lowered the RO capital costs, but increased the overall treatment costs to $0.52/1000 gal of finished water, again due to the need to install new pretreatment equipment. While using existing conventional treatment plants can potentially save millions of dollars in capital expenditures, the RO costs associated with using conventional treatment are significantly higher than with using either microfiltration or conventional treatment with ozone/biofiltration. Additionally, high membrane fouling rates associated with using conventional treatment may reduce this option's feasibility.

Commercialization Potential

To ensure commercial viability and the implementation of newly developed technology, project results will be published in refereed journals and presented at national conferences to water and wastewater industry professionals. The purpose of publications/presentations is to disseminate technical information to a broad range of industry representatives. Results for this study can then be incorporated into ongoing research and development activities throughout California, and the country. In addition, suppliers of membrane and membrane-related technologies will develop comparable products to maintain competitiveness in the industry.

Recommendations

Additional applied research is still needed to optimize the conventional treatment process with and without ozone/biofiltration. A better understanding of the improved performance under the ozone/biofiltration pretreatment and its effects on the NOM of the water are needed. Additional work is also needed to better understand the full effects of the interaction of different chemicals such as: coagulants (i.e. ferric, alum), disinfectants (i.e. chloramines), and antiscalants on the surface of the membrane.

It is recommended that for utilities which are designing new desalination plants, microfiltration is the optimal pretreatment technology which provides the best feed water for RO membranes, while minimizing fouling. However, additional work with conventional treatment processes may help water treatment plants use existing infrastructure as pretreatment to RO, thereby saving capital costs.

Benefits to California

This project, entitled *Electrotechnology Applications for Potable Water Production and Protection of the Environment*, was an integrated part of a larger program; the Desalination Research and Innovation Partnership (DRIP). The overall goal of the DRIP program is the cost-effective demineralization of CRW, as well as other water sources. Results from this study, as well as other interrelated studies, will enable local municipalities to adopt desalination technologies to treat current and previously unusable potable water supplies.

The primary economic benefit of the DRIP program is the reduction of societal damages to the public and private sectors due to high salinity of Colorado River water. An additional benefit is the reduction of energy usage to reduce the TDS of CRW over currently available technologies. These are broad societal, or public interest, benefits that conform to PIER goals. Each acre-foot of CRW treated by technologies derived from this project would require less energy than current desalination practices, or through importing low salinity water from Northern California. Additionally, technologies evaluated during this project may be applicable to other source waters in California. These include municipal wastewater, brackish groundwater, and agricultural drainage water.

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GLOSSARY

Colorado River water (CRW) - influent water source from Lake Mathews, California, the southern terminus for the Colorado River aqueduct system.

Energy dispersive spectroscopy (EDS) - A group of techniques used to analyze the atomic structure of materials. In laboratory instruments, dispersion of radiation often occurs by the use of a prism or diffraction grating. Normal dispersion occurs when the change in refractive index increases with increasing frequency (decreasing wavelength). When the reverse occurs, absorption takes place. The absorption of radiation by materials serves as the basis for a number of types of spectroscopic analyses.

Flux - The volume or mass of permeate passing through the membrane per unit area per unit time.

Fouling - The deposition of material such as colloidal matter, microorganisms, and metal oxides on the membrane surface or in its pores, causing a decrease in membrane performance.

Microfiltration (MF) - A pressure driven membrane process that separates particles as small as 0.1-μm-diameter from a feed stream by filtration. The smallest particle size removed is dependent of the pore size rating of the membrane.

Natural organic matter (NOM) - A heterogeneous mixture of organic matter that occurs ubiquitously in both surface water and groundwater, although its magnitude and character differ from source to source.

Normalized flux - The permeate flow rate through the membrane adjusted to constant operating conditions.

Not detected (ND) - Compounds not detected in samples analyzed

Not sampled (NS) - A sample was not collected to be analyzed.

Rejection - In a pressure-driven membrane process, a measure of the membrane's ability to retard or prevent passage of solutes and other contaminants through the membrane barrier.

Reverse osmosis (RO) - A pressure-driven membrane separation process that removes ions, salts, and other dissolved solids and nonvolatile organics. The separation capability of the process is controlled by the diffusion rate of solutes through the membrane barrier and by sieving. In potable water treatment, reverse osmosis is typically used for desalting, specific ion removal, and natural and synthetic organics removal.

Scale - Coating or precipitate deposited on surfaces.

Scanning electron microscopy (SEM) – Electron microscope techniques where an electron beam operates as a probe by being deflected across the surface of a specimen coated with gold and palladium.

Silt density index (SDI) - An empirical measure of the plugging characteristics of membrane feedwater based on passing the water through a membrane filter test apparatus containing a 0.45-micrometer pore diameter filter.

Specific flux - The permeate (water) flux divided by the net driving pressure.

State Project water (SPW) - influent water source from Northern California via the California State Water Project.

Trans-membrane pressure (TMP) - The net pressure loss across the membrane. For microfiltration and ultrafiltration with negligible osmotic pressure differential across the membrane, the hydraulic pressure differential from feed side to permeate side.

Total dissolved solids (TDS) - The weight per unit volume of solids remaining after a sample has been filtered to remove suspended and colloidal solids.

Total organic carbon (TOC) - A measure of the concentration of organic carbon in water, determined by oxidation of the organic matter into carbon dioxide. Total organic carbon includes all the carbon atoms covalently bonded in organic molecules.

TABLES AND FIGURES

Table 1. Commercial test membranes used during pilot- and full-scale testing

Code	Manufacturer	Membrane	Membrane Type
RO1	Dow Separation Processes	FilmTec Enhanced LE	Ultra-low-pressure
RO2	Koch Fluid Systems	TFC®-ULP	Ultra-low-pressure
RO3	Hydranautics	LFC1	Low-fouling composite
RO4	Hydranautics	ESPA3	Ultra-low-pressure
RO5	Hydranautics	ESPA1	Ultra-low-pressure

Table 2. Summary of project approach

	Pretreatment	Membrane Unit	Membrane Code
Pilot-Scale Testing	Conventional Treatment*	3-Element Membrane Test Unit	RO1
	Conventional Treatment with Ozone/Biofiltration*	3-Element Membrane Test Unit	RO1
	Microfiltration	24-Element Membrane Test Unit	RO2
Full-Scale Testing	F. E. Weymouth Filtration Plant*	3-Element Membrane Screening Unit	RO1 RO2 RO3
	Robert F. Skinner Filtration Plant*	3-Element Membrane Screening Unit	RO1 RO2 RO4
	Robert F. Skinner Filtration Plant**	3-Element Membrane Screening Unit	RO1 RO2 RO4 RO5

* Testing using aluminum sulfate coagulation
** Testing using ferric chloride coagulation

Table 3. Summary of pilot-scale pretreatment performance*

Parameter	RO Membrane Manufacturer's Guidelines	Conventional Treatment	Conventional Treatment with Ozone/Biofiltration	Microfiltration
Effluent Turbidity	< 1 NTU	0.10 NTU	0.08 NTU	0.05 NTU
Effluent Silt Density Index	< 5	3.1	2.4	0.83
Effluent Particles	NA	14 particles/mL	100 particles/mL	2 particles/mL
Free Chlorine	0 mg/L	0.02 mg/L	0.02 mg/L	0.02 mg/L
Effluent HPC (w/ Chloramines)	NA	37 cfu/mL	463 cfu/mL	4 cfu/mL
Operational Reliability	NA	Good	Good	Good

* All data given in average values
NA = Not available

Table 4. Pilot-scale pretreatment effluent water quality data*[†]

Parameter	Influent	Microfiltration	Conventional Treatment	Ozone Biofiltration
Alkalinity (mg/L as $CaCO_3$)	106	105	99	109
Total Hardness (mg/L as $CaCO_3$)	215	213	199	231
Total Dissolved Solids	475	463	473	491
Calcium (mg/L)	55	52	57	57
Magnesium (mg/L)	22	21	23	22
Potassium (mg/L)	3.6	3.5	3.5	3.7
Sodium (mg/L)	72	69	77	77
Nitrate (mg/L)	1.4	1.1	2.2	1.3
Silica (mg/L)	9.9	9.5	11	9
Chloride (mg/L)	69	68	79	180
Sulfate (mg/L)	166	162	160	180
Fluoride (mg/L)	0.22	0.21	0.20	0.24
Barium (µg/L)	76	73	77	76
Aluminum (µg/L)	39	6.8	ND	ND
Iron (µg/L)	64	9.25	ND	13
Strontium (µg/L)	730	725	746	795

* All values based on average flows
[†] All values calculated from averaged data
ND = Not detected

Table 5. Summary of reverse osmosis operating conditions during pilot-scale testing

Run No.	Pretreatment	Membrane Code	Operating Flux (gfd)	Specific Flux (gfd/psi)	Chloramines
1	Conventional Treatment	RO1	12	0.28	Yes
2	Conventional Treatment	RO1	13	0.28	Yes
3	Conventional Treatment	RO1	12	0.28	Yes
4	Conventional Treatment with Ozone/Biofiltration	RO1	21	0.36	Yes
5	Conventional Treatment with Ozone/Biofiltration	RO1	16	0.34	No
6	Microfiltration	RO2	17	0.23	Yes

Table 6. Summary of reverse osmosis performance given pilot-scale pretreatment type

Evaluation Criteria	Conventional Treatment*	Conventional Treatment with Ozone/Biofiltration	Microfiltration**
Specific Flux (gfd/psi)[†]	0.29	0.35	0.23
Normalized Operating Pressure (psi)[‡]	61	57	83
Energy Usage (kWh/1000 gal)[§]	0.55	0.52	0.75
Salinity Rejection (Percent)	98	98	93
Permeate Water Quality (mg/L TDS)	10	11	34
Cleaning Frequency (Months)	1	2	2-3
Operational Reliability	Poor	Moderate	Good

* Average values of three RO runs

[†] Normalized to 25ºC

[‡] Assume flux = 15 gfd, temperature = 25ºC

[§] Pump efficiency = 80 percent

** Microfiltration data collected using different RO membranes, hence differences in operational parameters are not a function of pretreatment

Table 7. Energy dispersive spectroscopy analysis of pilot-scale conventionally pretreated reverse osmosis membranes*

Ion	Conventional Treatment	Ozone/ Biofiltration	Microfiltration
Aluminum	ND	4	18
Barium	ND	ND	ND
Calcium	ND	33	ND
Magnesium	ND	6	ND
Phosphorous	ND	5	11
Chloride	ND	ND	ND
Iron	ND	24	ND
Silica	ND	11	ND
Sulfur	> 99	15	71

* All data given as percent w/w.
ND = Not detected

Table 8. Salinity removal of reverse osmosis membranes per pretreatment process*[†]

Parameter	Microfiltration Rejection (%)	Conventional Treatment Rejection (%)	Ozone Biofiltration Rejection (%)
Alkalinity	90	96	96
Total Hardness	98	>99	>99
Total Dissolved Solids	93	98	98
Calcium	98	>99	>99
Magnesium	97	>99	>99
Potassium	84	97	96
Sodium	85	97	97
Nitrate	56	89	87
Silica	96	96	95
Chloride	86	97	97
Sulfate	98	98	99
Fluoride	84	91	96
Barium	97	>99	>99
Aluminum	82	55	95
Iron	ND	79	ND
Strontium	98	>99	>99

* All values based on average flows
[†] All values calculated from averaged data
ND = Not detected

Table 9. Effects of treatment on natural organic matter[†]

Pretreatment	Parameter	Pretreatment Influent	Pretreatment Effluent	RO Permeate	RO Brine
Microfiltration	TOC (mg/L)	2.6	2.5	0.2	26
	SUVA (L/mg-m)	2.0	2.2	4.4	2.0
	HPC (cfu/mL)	2,230	4	7,260	10,000
Conventional Treatment	TOC (mg/L)	3.1	2.8	ND	17
	SUVA (L/mg-m)	1.9	1.9	--	1.4
	HPC (cfu/mL)	5,010	37	2	290
Ozone/ Biofiltration	TOC (mg/L)	2.7	2.3	ND	13
	SUVA (L/mg-m)	1.5	1.1	--	1.1
	HPC (cfu/mL)	11,330	463	17	3,860

[†] All data given in average values

Table 10. Full-scale pretreatment effluent water quality data*[†]

Parameter	F. E. Weymouth	Robert F. Skinner	
	Alum coagulation	Alum coagulation	Ferric chloride coagulation
Alkalinity (mg/L)	106	109	100
Total Hardness (mg/L)	235	235	230
Total Dissolved Solids (mg/L)	505	497	483
Total Organic Carbon (mg/L)	2.7	2.4	2.6
SUVA (L/mg-m)	1.4	1.9	1.9
Calcium (mg/L)	57	58	56
Magnesium (mg/L)	22	23	22
Potassium (mg/L)	3.7	3.6	3.9
Sodium (mg/L)	72	73	68
Nitrate (mg/L)	0.72	1.2	1.1
Silica (mg/L)	9.0	9.6	9.5
Chloride (mg/L)	67.6	72.6	69
Sulfate (mg/L)	186.3	181	171
Fluoride (mg/L)	0.26	0.22	0.21
Barium (μg/L)	77.9	83.4	73
Aluminum (μg/L)	230	127	16
Iron (μg/L)	ND	ND	ND
Strontium (μg/L)	765	865	720

* All values based on average flows

[†] All values calculated from averaged data

ND = Not detected (below 20 μg/L for iron)

Table 11. Operation observations for F.E. Weymouth reverse osmosis testing

RO Run Time (hours)	Description
0 – 369	The RO unit was started with fresh 4-in. diameter elements. No evidence of specific flux loss was evident, though all three membranes showed decreasing salt rejection.
369 – 530	The antiscalant was changed from a phosphonate-based antiscalant (Permacare, Permatreat 191) to a polyorganic-based antiscalant (Professional Water Treatment [PWT], Spectraguard™, Escondido, Calif.). Immediately after the change in antiscalant, two of the three parallel membranes showed a 60 percent decrease in specific flux (RO1 and RO2). Each of the fouled membranes were traditional ultra-low-pressure polyamide membranes, while the remaining unfouled membrane (RO3) was a new experimental low-fouling composite, polyamide membrane. While only two RO membranes demonstrated reductions in specific flux, all three membranes continued to exhibit a decline in salt rejection—for a total decrease in salt rejection of at least a 3 percent.
530 – 972	Upon acid and caustic cleaning of the membranes, the specific flux for each membrane returned to the initial conditions. However, salt rejection for each membrane showed only approximately 50 percent recovery over initial conditions. Continued testing using the polyorganic-based antiscalant showed at least a 50 percent reduction in specific flux for RO1 and RO2, and a 40 percent reduction in specific flux for RO3. Salt rejection for all three membranes also showed a continued declining trend. Autopsy of RO2 showed significant inorganic deposits comprising mostly of aluminum, iron, and silica; suggesting deposition of aluminum and iron silicates.
972 – 1,130	RO1 and RO3 were chemically cleaned with acid and caustic solutions. The antiscalant was changed back to the original phosphonate-based antiscalant. Specific membrane flux again returned to initial conditions, though salt rejection showed an even lower degree of recovery over the first cleaning cycle. Both membranes continued to show declines in specific flux and salt rejection over the 170 hrs of operation, though RO3 showed a lower decline in specific flux than RO1.
1,130 – 1,663	Membrane RO2 was replaced with an identical, new element at 1,130 hrs of operation and RO3 was replaced with RO4. RO1 was left in the unit without cleaning despite already exhibiting a 30 percent reduction in specific flux and a 1.4 percent reduction in salt rejection. All membranes continued to show similar declines in specific flux and salt rejection over 500 hrs of operation. RO unit shutdowns at 1,310 and 1,471 hrs of operation appeared to partially restore specific flux, although the downward trends continued after restarting the RO unit. A 5-μm prefilter was installed at 1,485 hrs of operation with no effect on the deterioration of specific flux or salt rejection.
1,663 – 2,203	All three RO elements (RO1, RO2, and RO4) were chemically cleaned with acid and caustic solutions. As per the previous cleaning cycles, the specific flux for all elements returned to initial conditions, though the salt rejection continued to show decreasing recovery. Continued testing over 540 hrs showed similar reductions in specific flux and salt rejection.

Table 12. Energy dispersive spectroscopy analysis of full-scale conventionally treated reverse osmosis membranes*

Ion	F. E. Weymouth Alum Coagulation	Robert F. Skinner	
		Alum Coagulation	Ferric Chloride Coagulation
Aluminum	25	32	5
Phosphorous	2	20	ND
Barium	ND	ND	ND
Calcium	ND	5.5	ND
Chloride	2	4.6	8
Iron	2	ND	7
Magnesium	5	ND	ND
Silica	16	15	11
Sulfur	28	24	68

* All data given as percent w/w.
ND = Not detected

Table 13. Energy dispersive spectroscopy analysis of Robert F. Skinner treated reverse osmosis membranes with and without chloramines*

Ion	With Chloramines	Without Chloramines
Aluminum	ND	7.6
Phosphorous	ND	13
Barium	ND	ND
Calcium	4.2	17
Chloride	4.2	6.5
Iron	6.8	8.3
Magnesium	ND	ND
Silica	20	14
Sulfur	65	34

* All data given as percent w/w.
ND = Not detected

Table 14. Pretreatment process cost detail in thousands of dollars for a 100-mgd plant

Cost Component	Microfiltration	Conventional Treatment	Conventional Treatment with Ozone/Biofiltration
		Pretreatment	
Energy ($/year)	786	285	450
Maintenance Mat'l ($/year)	1,521	161	229
Labor ($/year)	1670	1,047	1,186
Chemicals ($/year)	142	834	1671
Annual O&M Cost ($/year)	4,119	2,327	3,536
Unit O&M Cost ($/1,000 gal)	0.17	0.10	0.14
Total Capital Cost ($)	58,000	75,610	84,100
Annual Capital Cost ($/year)	5,055	6,592	7,332
Unit Capital Cost ($/1,000 gal)	0.21	0.27	0.30
Total Annual Cost ($/year)	9,174	8,919	10,868
Total Unit Cost ($/1000 gal)	0.38	0.37	0.44

Table 15. Assumed values used to calculate reverse osmosis process costs

Parameter	Microfiltration	Conventional Treatment	Conventional Treatment w. Ozone/ Biofiltration
Applied Feed Pressure*	140 psi	140 psi	140 psi
Permeate Pressure	10 psi	10 psi	10 psi
RO Membrane Fouling Allowance	15 percent	15 percent	15 percent
Feed TDS	750 mg/L	750 mg/L	750 mg/L
Product Recovery	85 percent	85 percent	85 percent
Membrane Flux	15 gal/ft^2/day	10 gal/ft^2/day	12 gal/ft^2/day
Chemical Cost	\$0.06/1000 gal of permeate	\$0.06/1000 gal of permeate	\$0.06/1000 gal of permeate
Pump Efficiency	0.80	0.80	0.80
Energy Cost	\$0.06/kWh	\$0.06/kWh	\$0.06/kWh
Capital Cost	\$0.85/gal/day installed capacity	\$0.85/gal/day of installed capacity	\$0.85/gal/day installed capacity
Spare Capital Equipment	\$0.15/gal/day installed capacity	\$0.15/gal/day of installed capacity	\$0.15/gal/day installed capacity
O&M Labor	\$0.03/1000 gal of permeate	\$0.03/1000 gal of permeate	\$0.03/1000 gal permeate
Filter replacement & Other Materials	\$0.10/1000 gal of permeate	\$0.10/1000 gal of permeate	\$0.10/1000 gal of permeate
Membrane Life	5 years	5 years	5 years
Membrane Type	Ultra-low-pressure polyamide RO	Ultra-low-pressure polyamide RO	Ultra-low-pressure polyamide RO
Element Area	380 ft^2	380 ft^2	380 ft^2
Membrane Cost	\$1.58/ft^2	\$1.58/ft^2	\$1.58/ft^2
Interest Rate	6 percent	6 percent	6 percent
Amortization Period	20 years	20 years	20 years

*Based on 5-yr old membrane element with 15 percent fouling at average feed temperature (64°F, 17.8°C)

Table 16. Reverse osmosis process cost detail in thousands of dollars for a 100-mgd RO plant

Cost Component	Pretreatment		
	Microfiltration	Conventional Treatment	Conventional Treatment with Ozone/Biofiltration
Energy ($/year)	4,845	4,845	4,845
Labor ($/year)	1,680	1,680	1,680
Chemicals ($/year)	1,972	1,972	1,972
Membrane Replacement ($/year)	2,100	2,632	2,198
Miscellaneous ($/year)	3,488	3,488	3,488
Contingency ($/year)	--	--	--
Make-Up Water ($/year)	5,108	5,108	5,108
Annual O&M ($/year)	**14,084**	**14,616**	**14,182**
Unit O&M Cost ($/1000 gal)	**0.39**	**0.41**	**0.40**
RO Capital ($)	144,364	178,535	161,721
Brine Pipeline Capital ($)	20,500	20,500	20,500
Total RO Cost ($)	**164,864**	**199,035**	**182,221**
Annual RO Capital Cost ($/year)	**14,373**	**17,353**	**15,887**
Unit Capital Cost ($/1000 gal)	**0.39**	**0.48**	**0.44**
Total Annual RO System Cost ($/year)	**28,457**	**31,969**	**30,069**

Table 17. Capital and operating costs for 300-mgd split-flow treatment plant with 100 mgd RO treatment

Cost Component	RO Pretreatment Type		
	Microfiltration (Split-Flow)	Conventional Treatment (Full-Flow)	Conventional Treatment with Ozone/ Biofiltration (Full-Flow)
Existing Treatment Energy Consumption (kWh/1000 gal)	0.09	0.09	0.09
Existing Treatment Capital Cost ($/1000 gal)	0.00	0.00	0.00
Existing Treatment O&M Cost ($/1000 gal)	0.08	0.09	0.09
Additional Pretreatment Energy Consumption (kWh/1000 gal)	0.44	--	0.13*
Additional Pretreatment Capital Cost ($/1000 gal)	0.21	--	0.12†
Additional Pretreatment O&M Cost ($/1000 gal)	0.17	--	0.03
RO Energy Consumption (kWh/1000 gal)	1.27	1.27	1.27
RO Amortized Capital Cost ($/1000 gal)	0.39	0.48	0.44
RO O&M ($/1000 gal)	0.39	0.41	0.40
Total Energy Consumption‡ (kWh/1000 gal of finished water)	**0.63**	**0.51**	**0.64**
Total Treatment Costs‡ ($/1000 gal of finished water)	**0.44**	**0.39**	**0.52**

* Assuming 2.0 mg/L O_3 and 7.5 kWh/Lb. of O_3

† Capital costs for retrofitting an existing conventional treatment plant (not shown in Table 12)

‡ Assumes only one-third of total flow is desalted.

	Pretreatment	1999												2000											
		J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
Pilot-Scale Testing	Conventional Treatment*														▨	▨	▨								
	Conventional Treatment with Ozone/Biofiltration*							▨	▨	▨	▨	▨	▨												
	Microfiltration																			▨	▨	▨	▨	▨	
Full-Scale Testing	F.E. Weymouth Filtration Plant*								▨	▨	▨													
	Robert A. Skinner Filtration Plant Part I*											▨	▨											
	Robert A. Skinner Filtration Plant Part II**														▨	▨	▨	▨	▨		▨	▨	▨	▨	▨

* Testing using aluminum sulfate coagulation

** Testing using ferric chloride coagulation

Figure 1. Experimental schedule
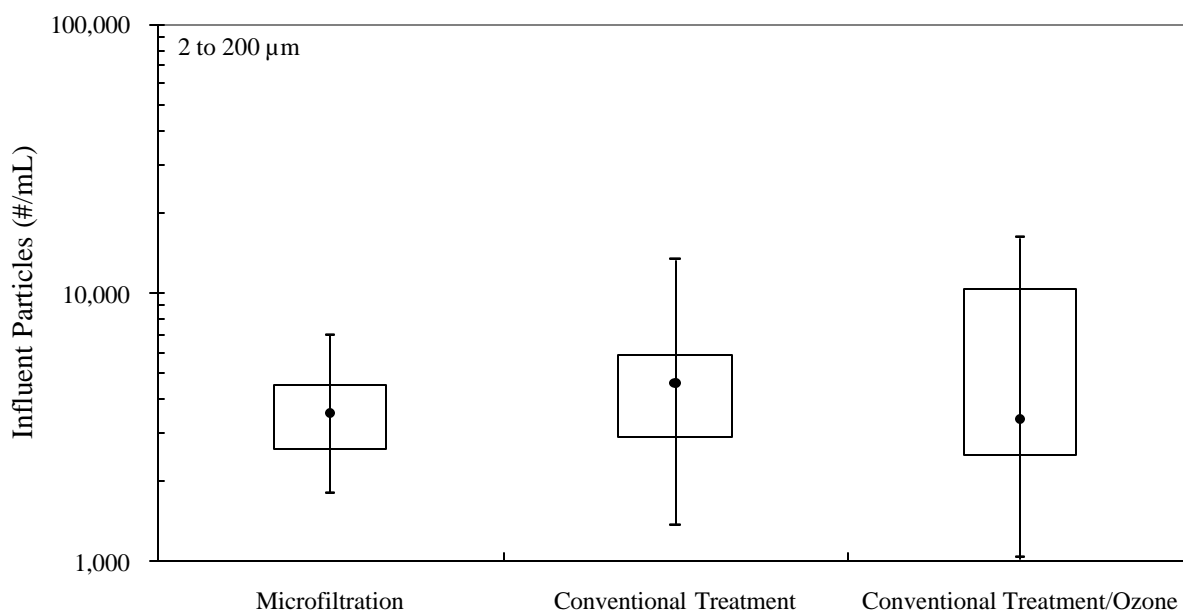
Figure 2. Pilot-scale pretreatment influent particle count data
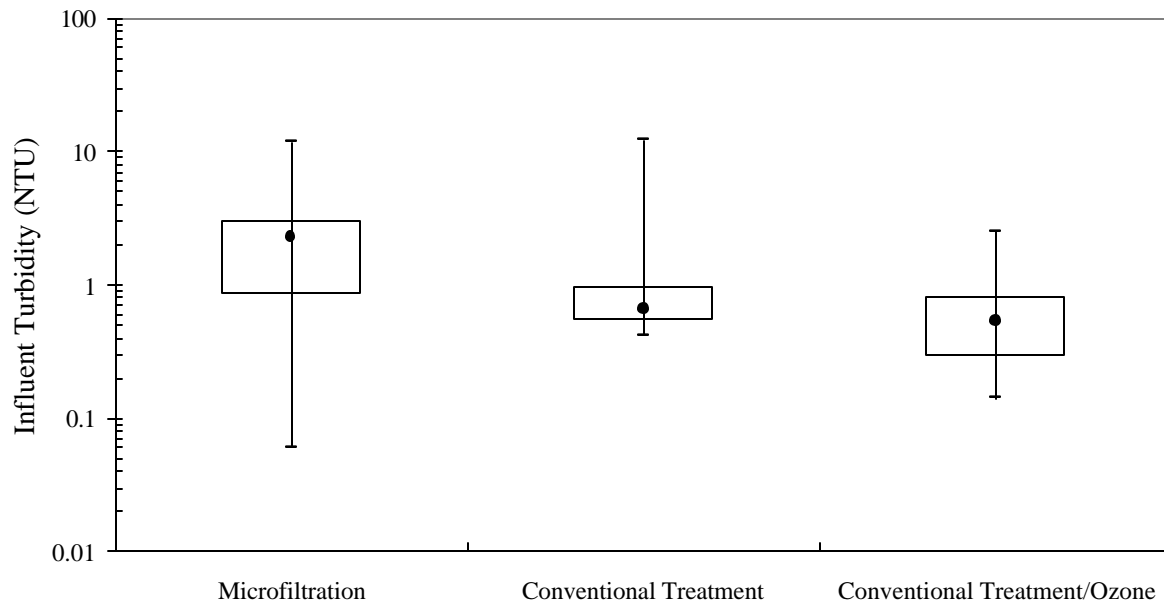
Figure 3. Pilot-scale pretreatment influent turbidity data
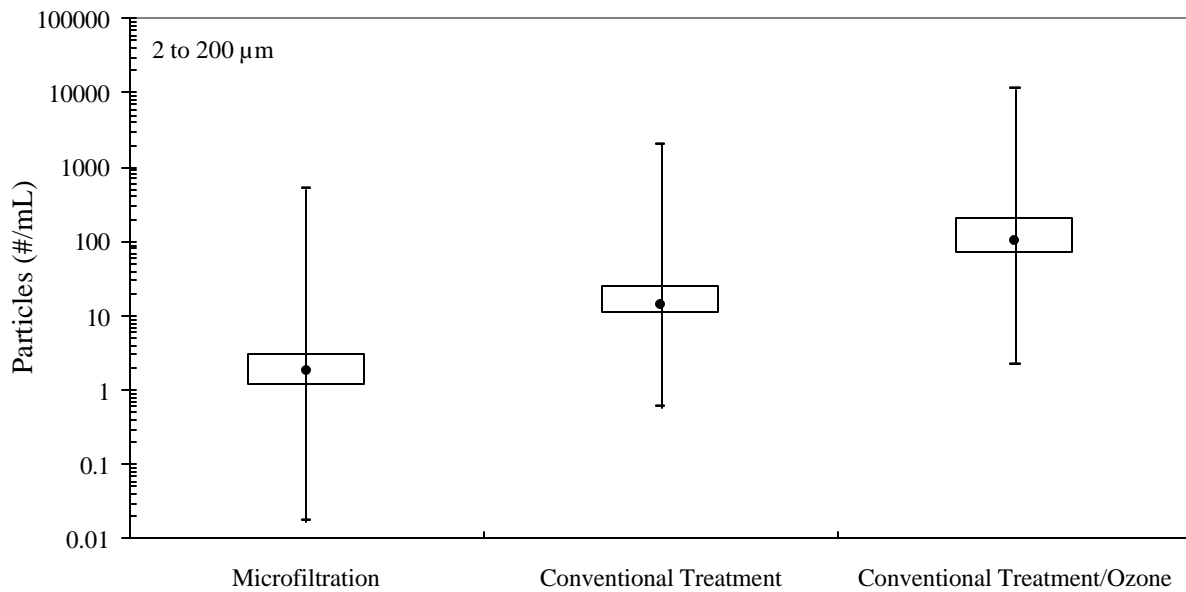
Figure 4. Pilot-scale pretreatment effluent particle count data
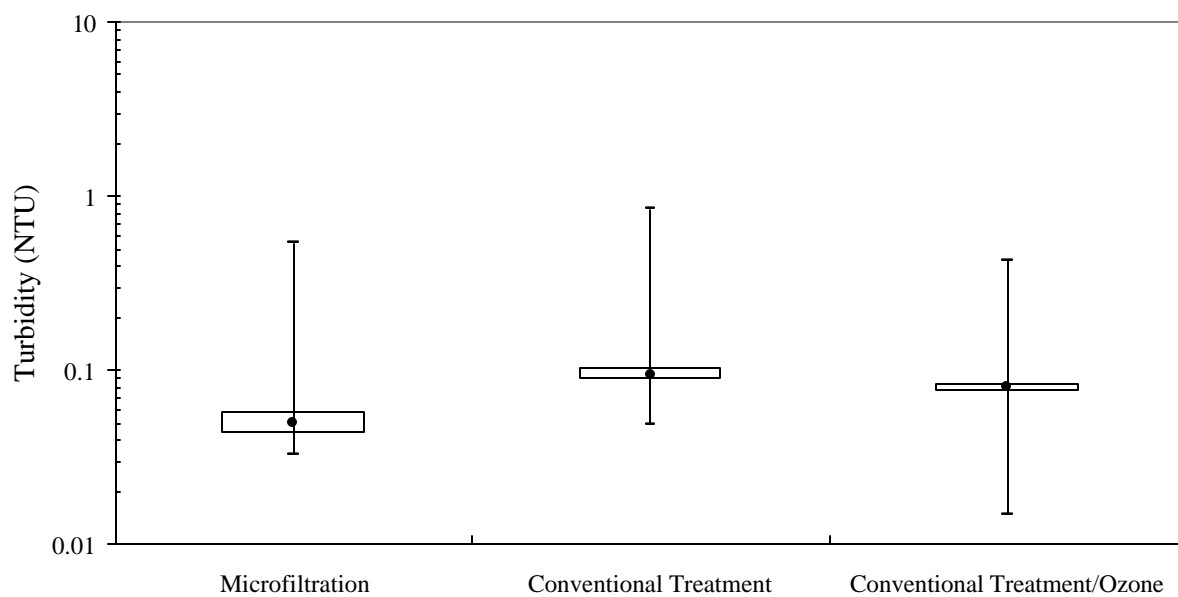
Figure 5. Pilot-scale pretreatment effluent turbidity data
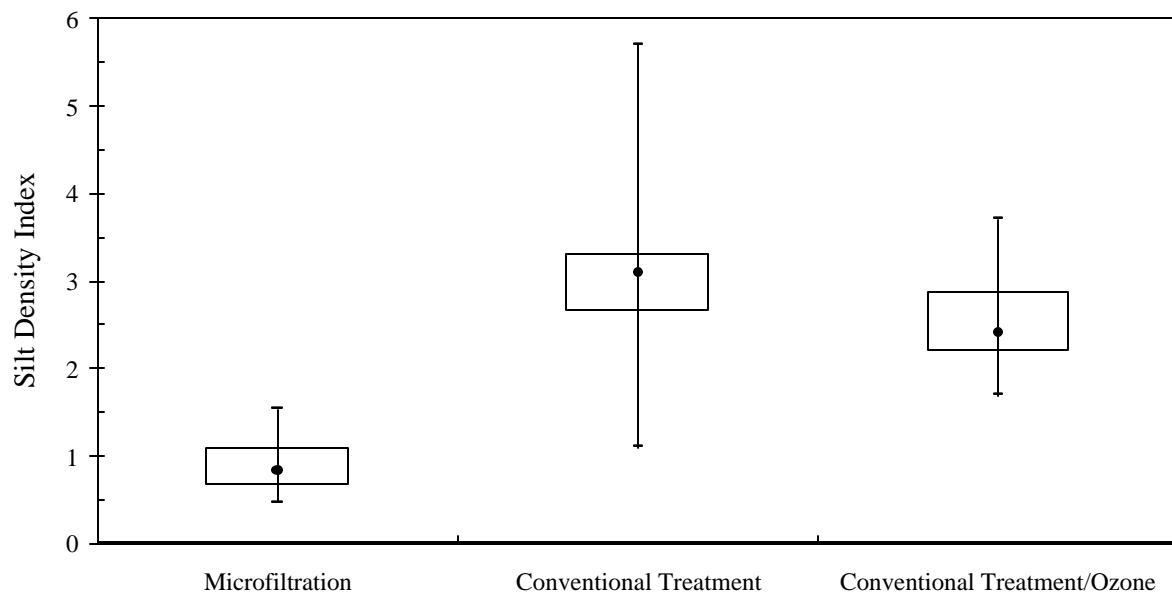
Figure 6. Pilot-scale pretreatment effluent silt density index data
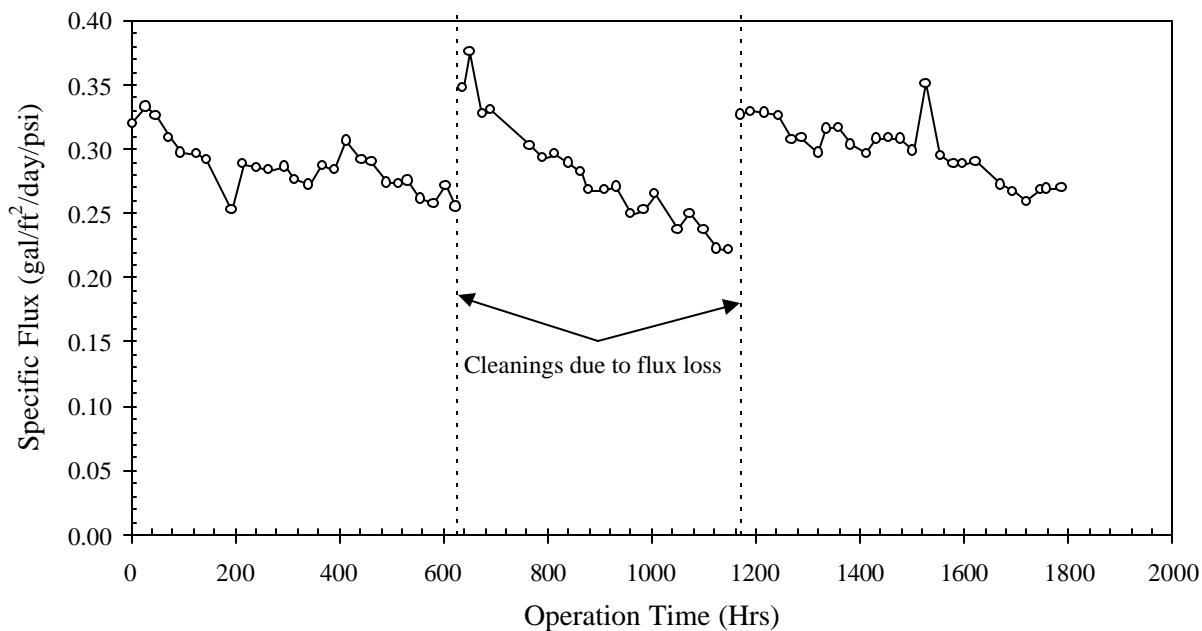
Figure 7. Specific membrane flux using conventional treatment
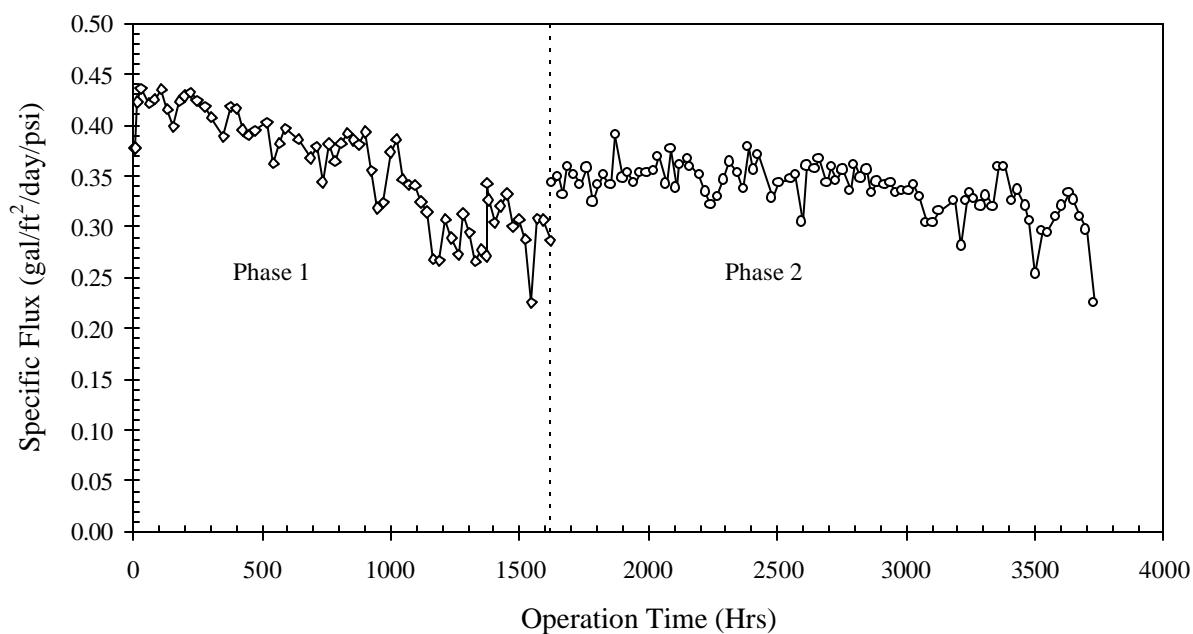
Figure 8. Specific membrane flux using conventional treatment with ozone/biofiltration: Phase 1 with chloramines, Phase 2 without chloramines
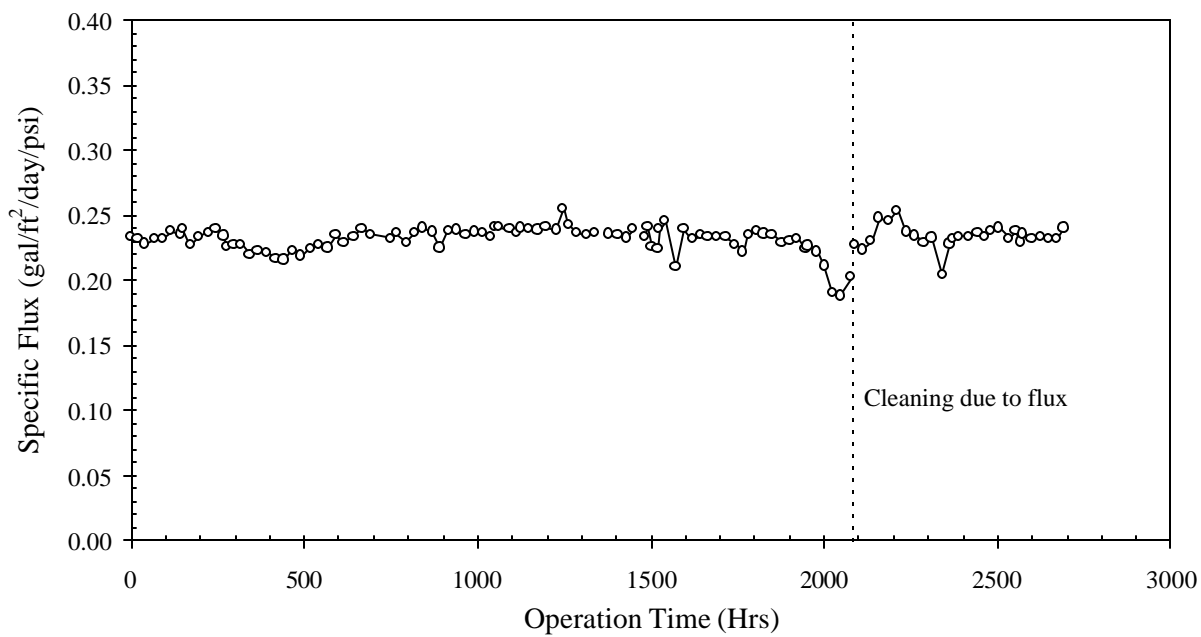
Figure 9. Specific membrane flux using microfiltration
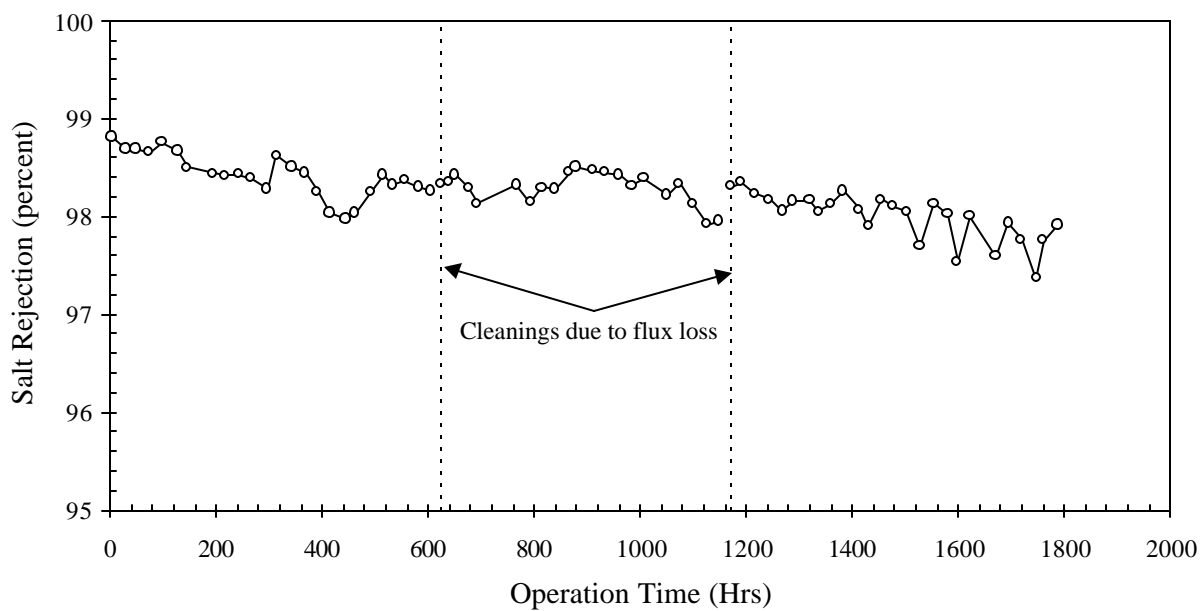
Figure 10. Membrane salt rejection using conventional treatment
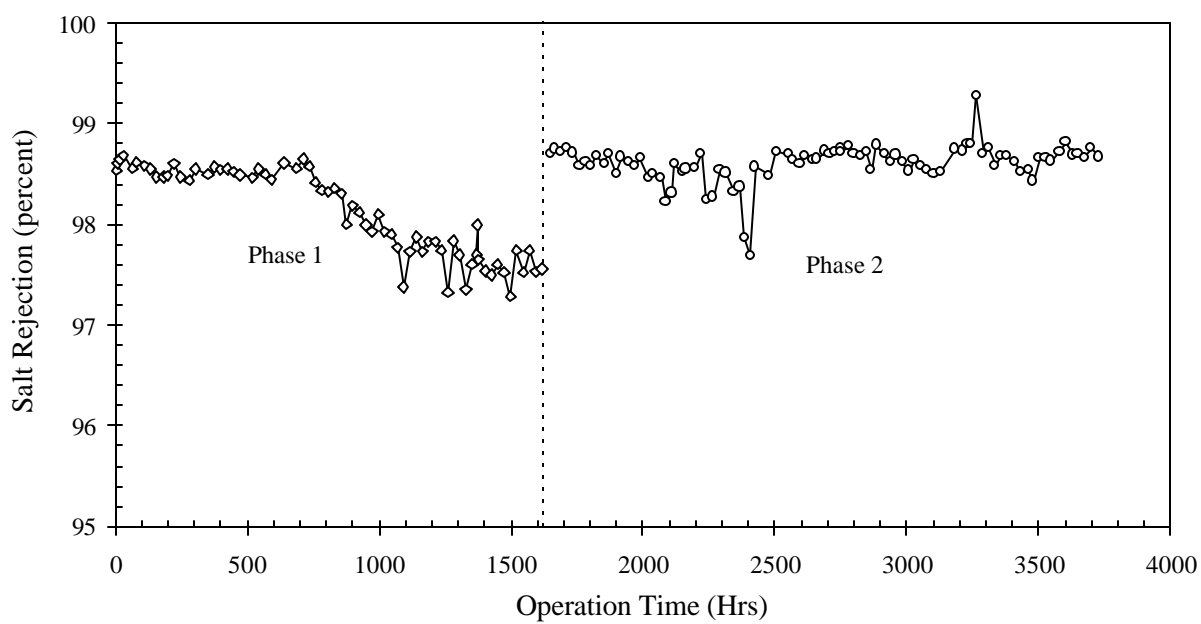
Figure 11. Membrane salt rejection using conventional treatment with ozone/biofiltration
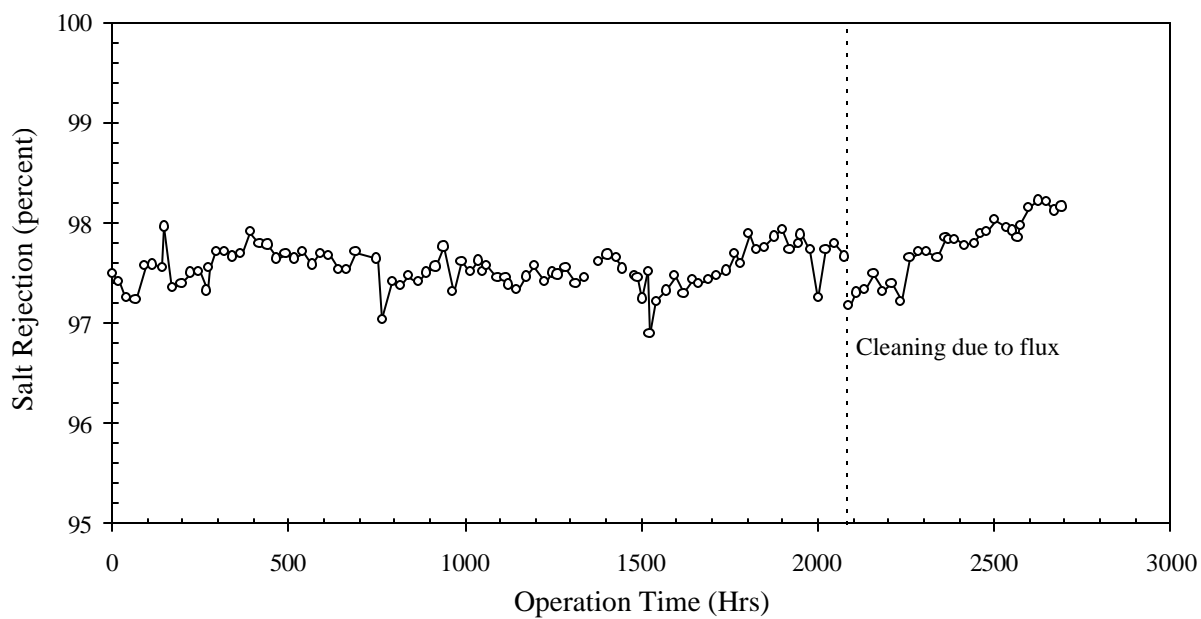
Figure 12. Membrane salt rejection using microfiltration

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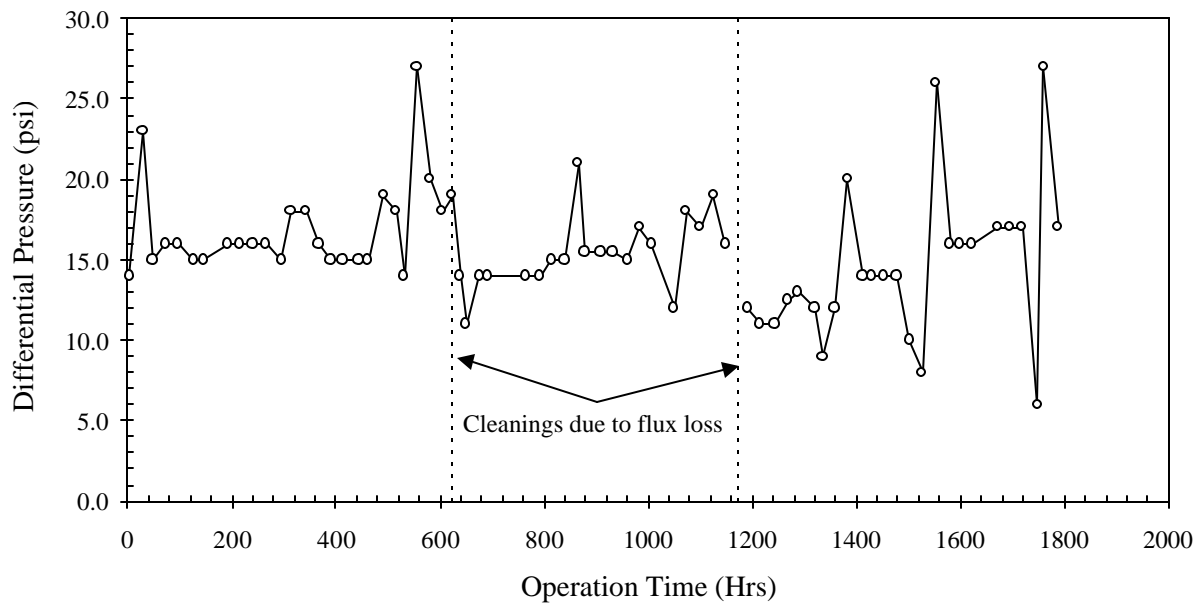
Figure 13. Differential pressure of membranes for conventional treatment
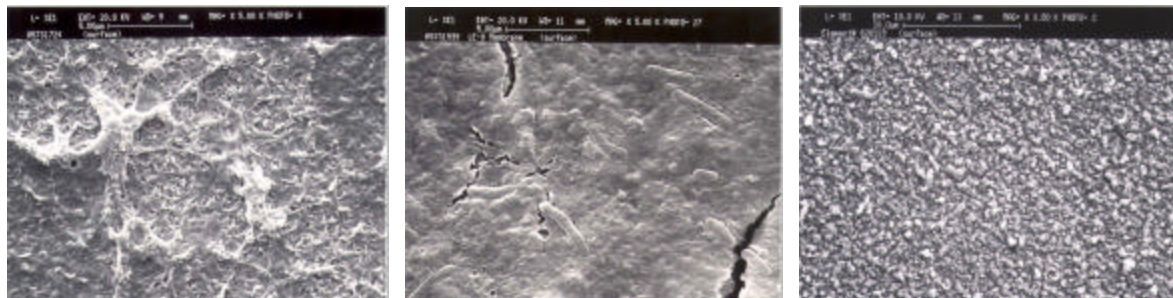
Conventional Treatment   Ozone/Biofiltration   Microfiltration

Figure 14. Plan view SEM micrographs of lead reverse osmosis membranes
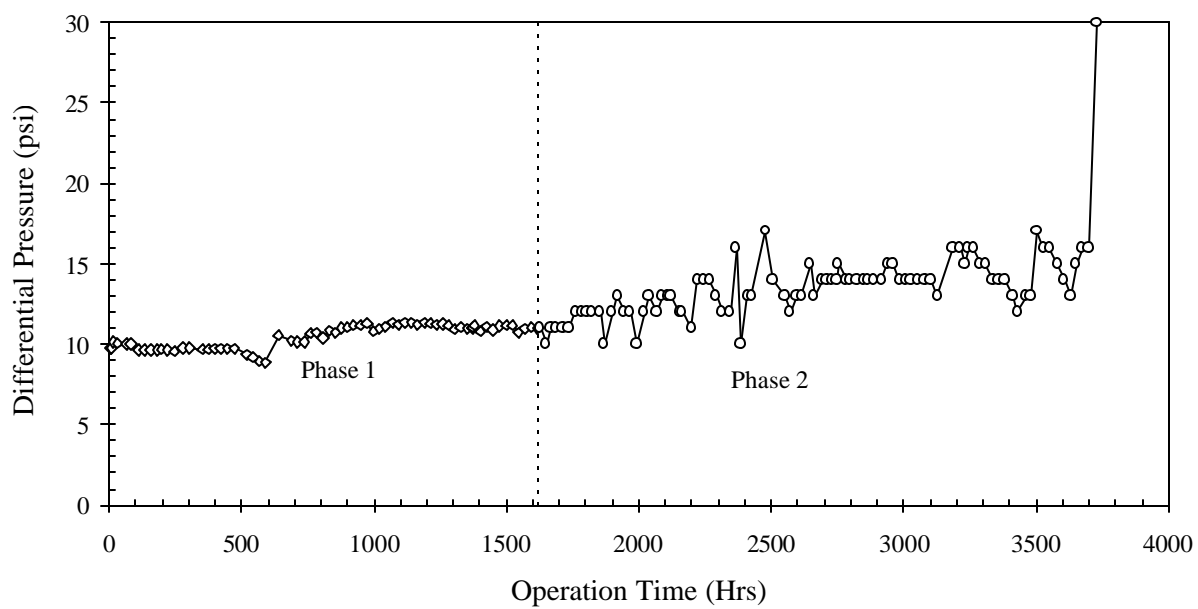
Figure 15. Differential pressure of membranes for ozone/biofiltration
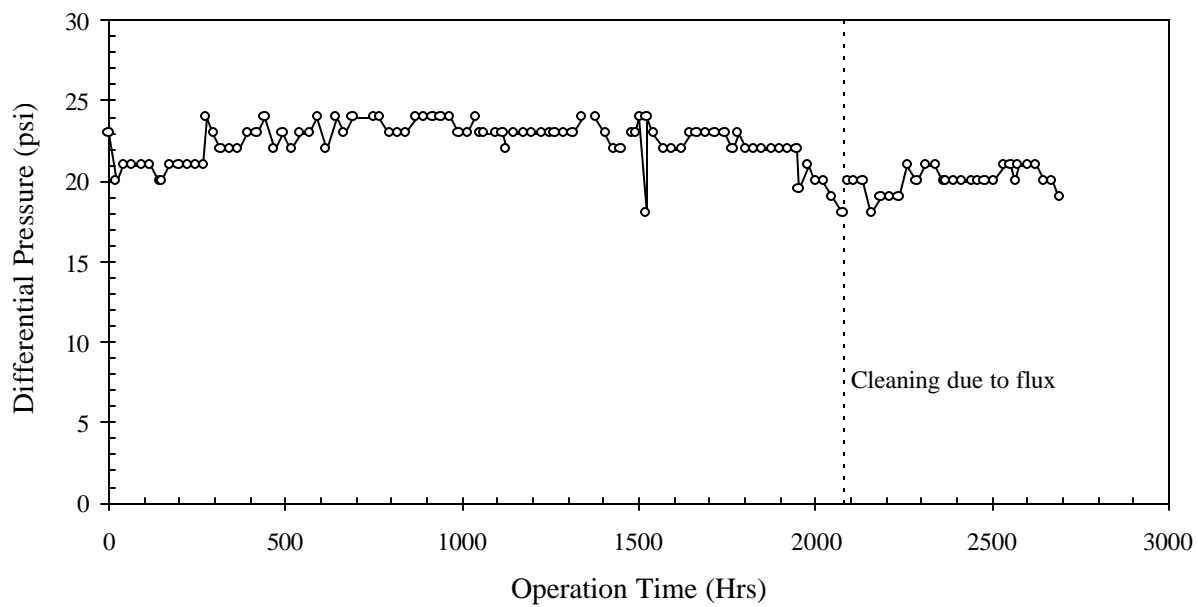
Figure 16. Differential pressure of membranes for microfiltration
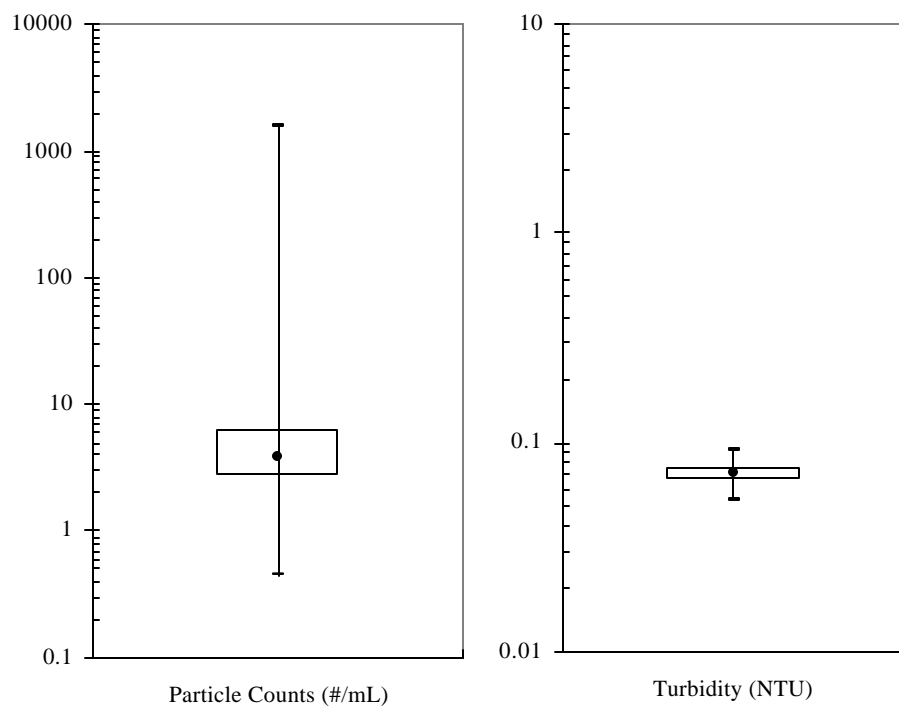
Figure 17. F. E. Weymouth Filtration Plant effluent water quality data: (a) particle counts; (b) turbidity
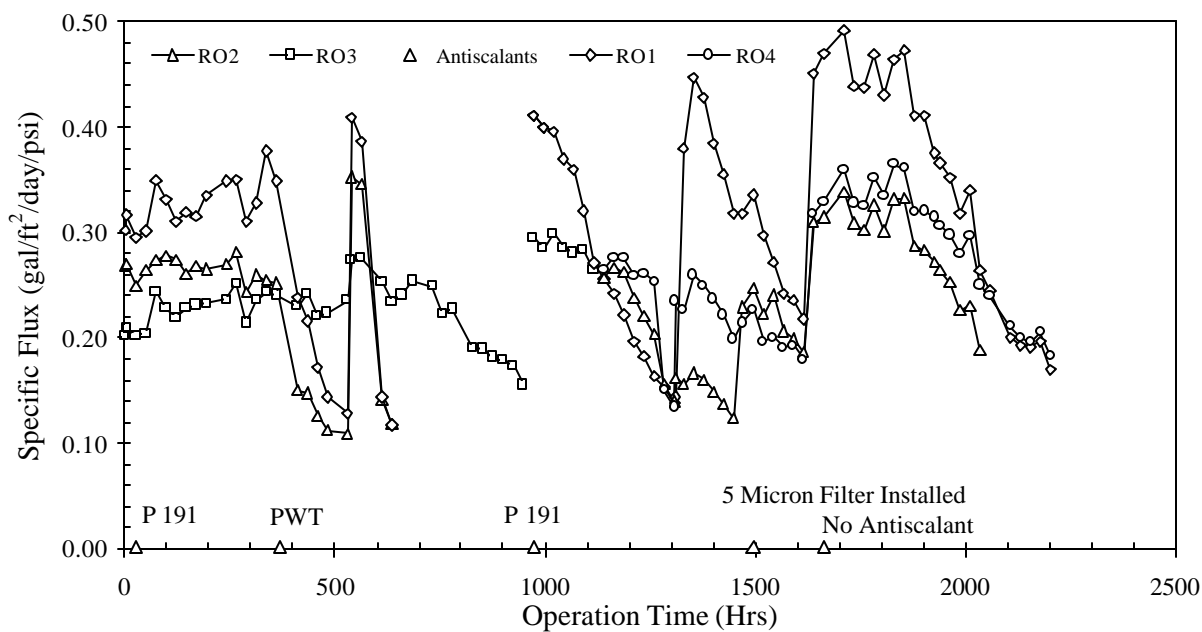
Figure 18. Specific membrane flux using F. E. Weymouth effluent
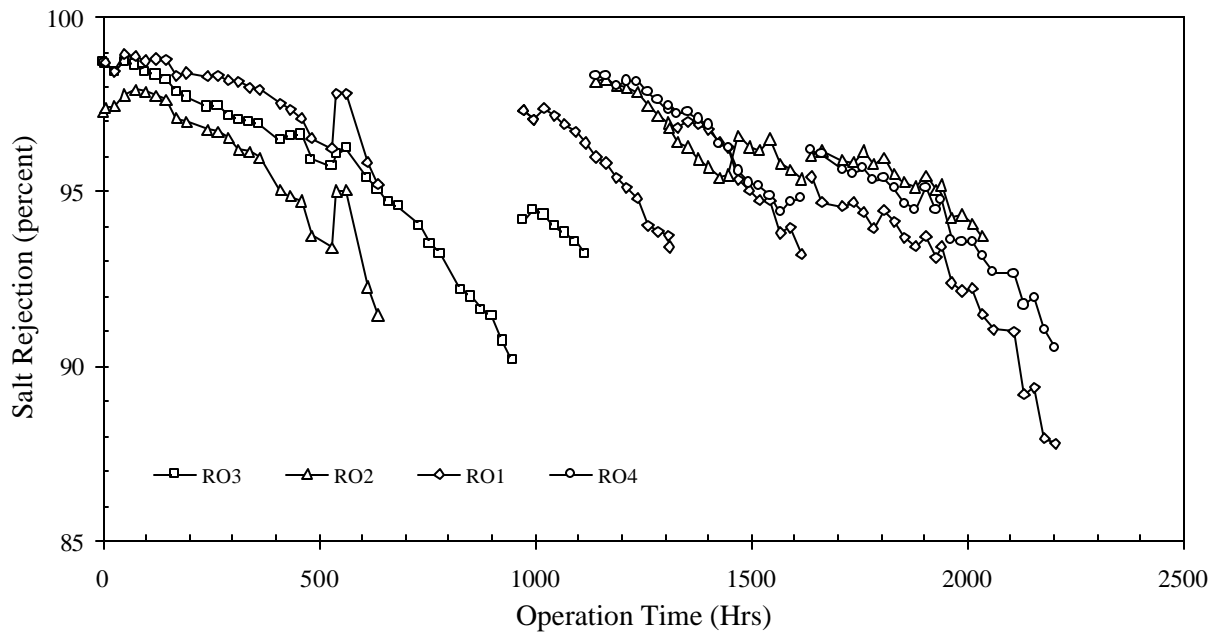
Figure 19. Salt rejection of reverse osmosis membrane using F. E. Weymouth effluent
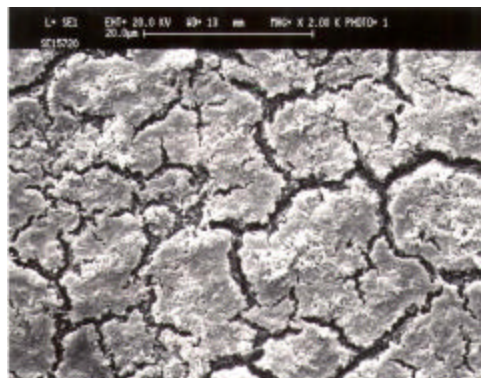
Figure 20. SEM micrograph of reverse osmosis membrane using F. E. Weymouth plant effluent
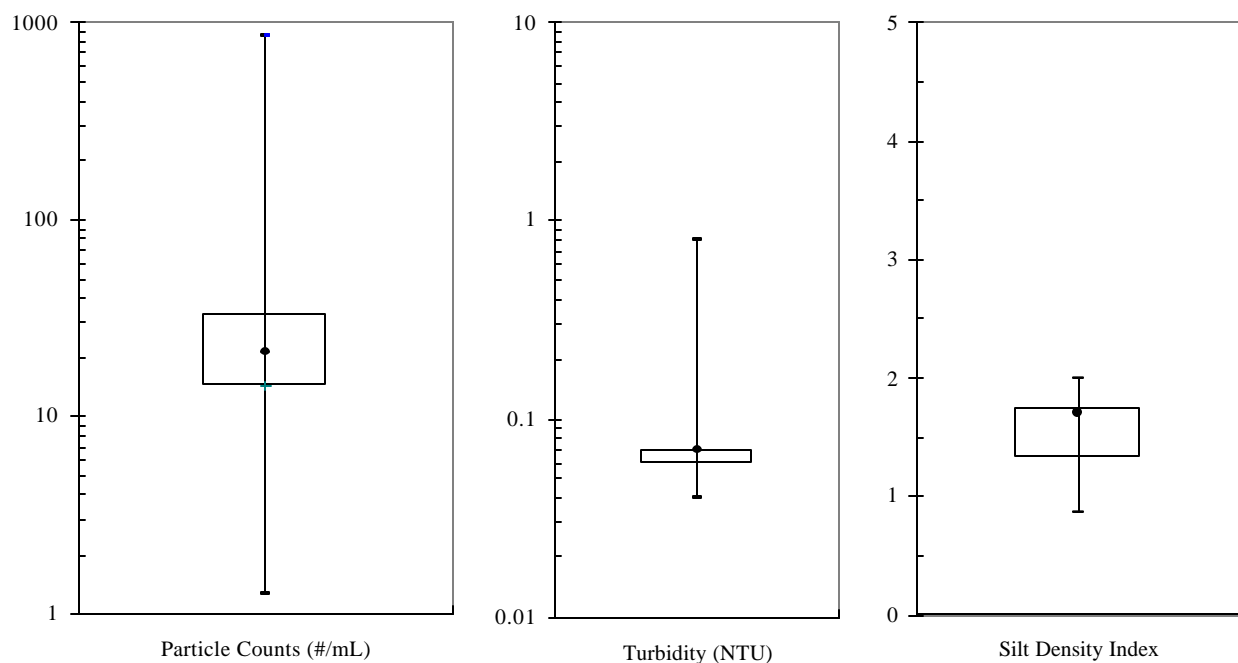
Figure 21. Robert F. Skinner Filtration Plant effluent water quality data: (a) particle counts; (b) turbidity; (c) silt density index
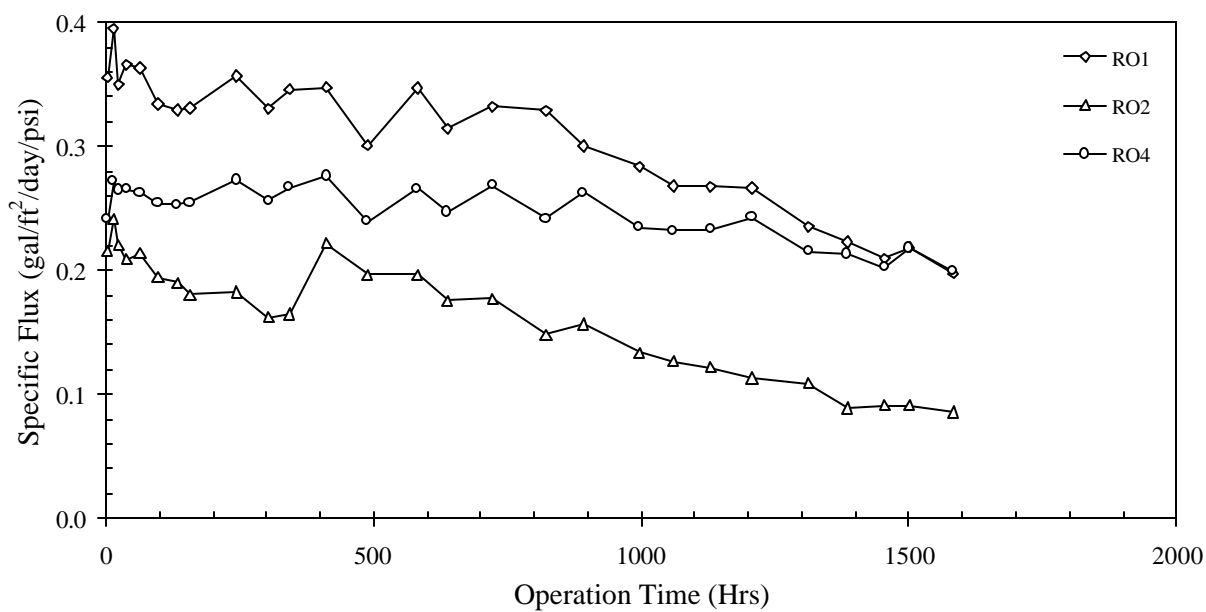
Figure 22. Specific membrane flux using Robert F. Skinner Filtration Plant effluent with aluminum sulfate and chloramines

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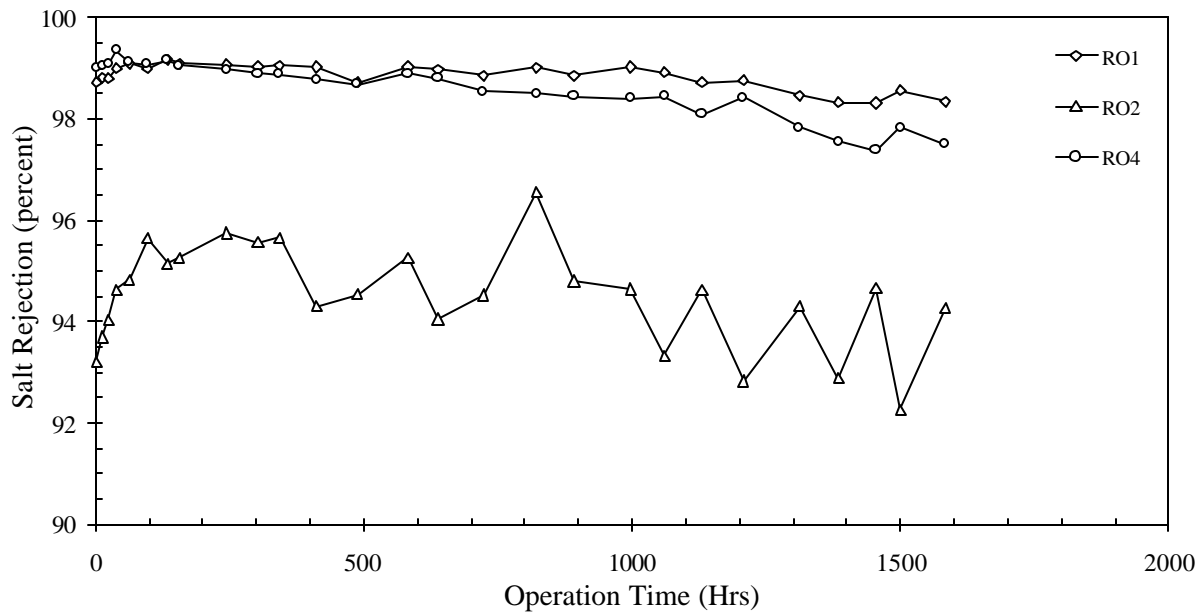
Figure 23. Salt rejection using Robert F. Skinner Filtration Plant effluent with aluminum sulfate and chloramines
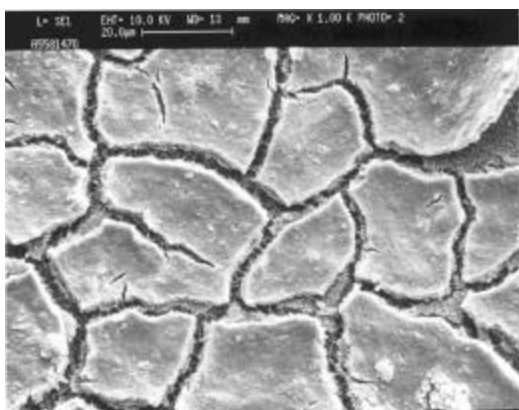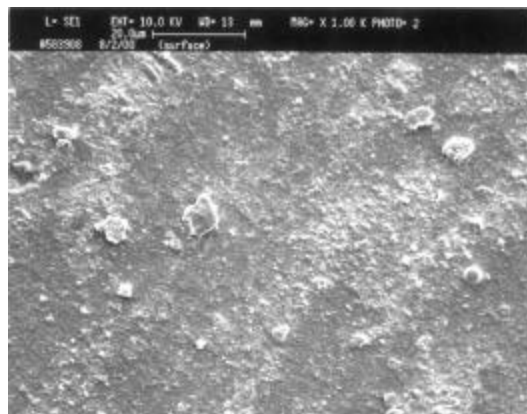
(a)   (b)

Figure 24. SEM micrographs of fouled reverse osmosis membranes using Robert F. Skinner Filtration Plant effluent with chloramines: (a) using alum coagulant; (b) using ferric chloride coagulant
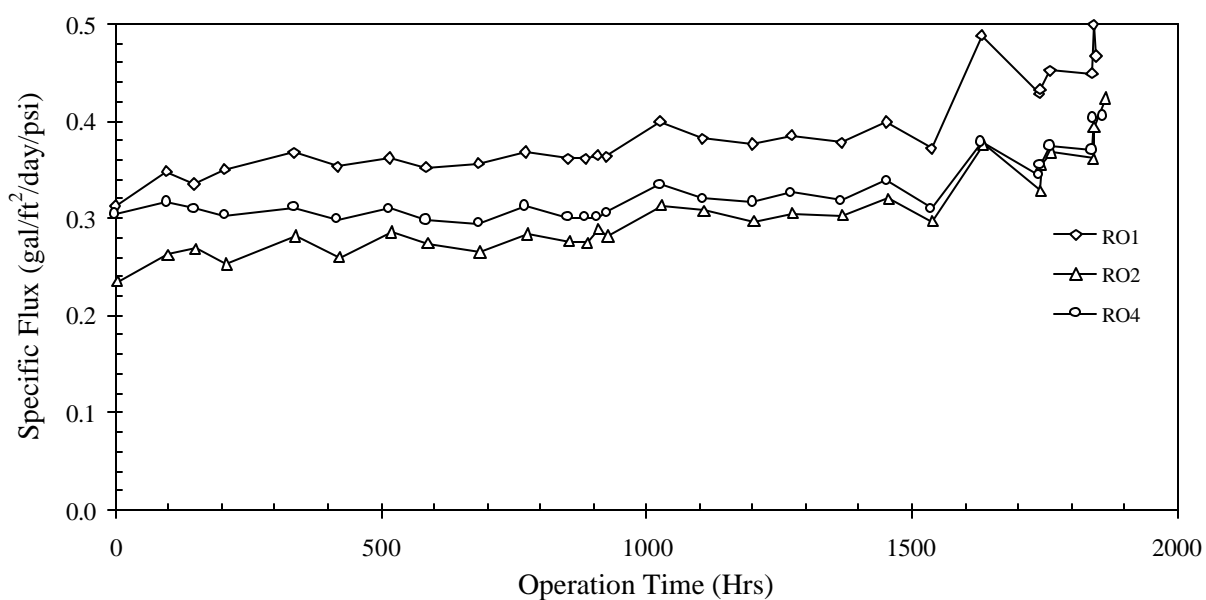
Figure 25. Specific membrane flux using Robert F. Skinner Filtration Plant effluent with ferric chloride and chloramines
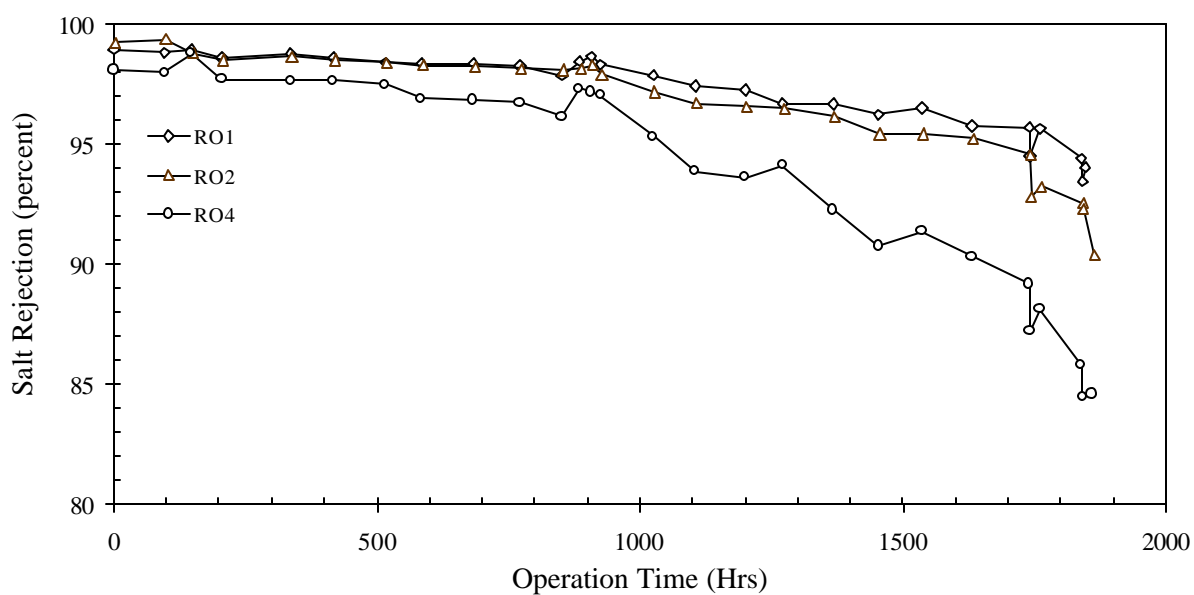
Figure 26. Salt rejection using Robert F. Skinner Filtration Plant effluent with ferric chloride and chloramines
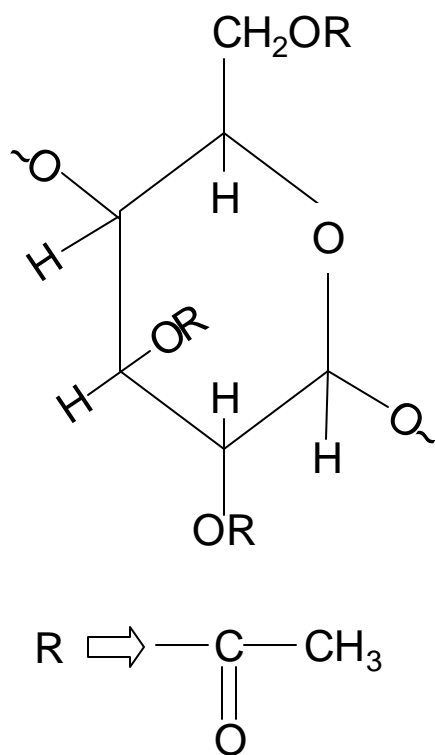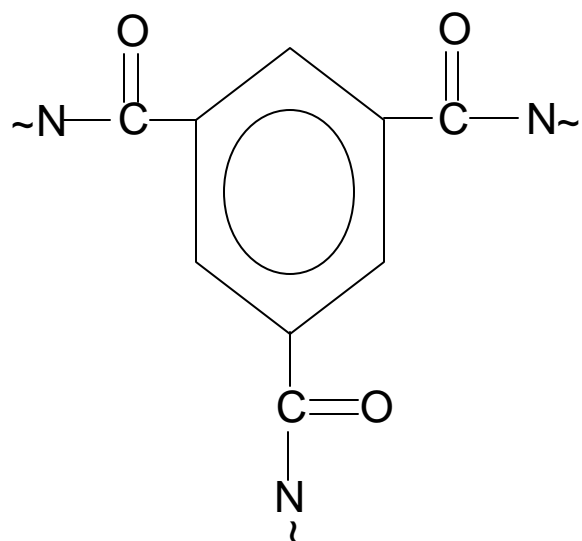
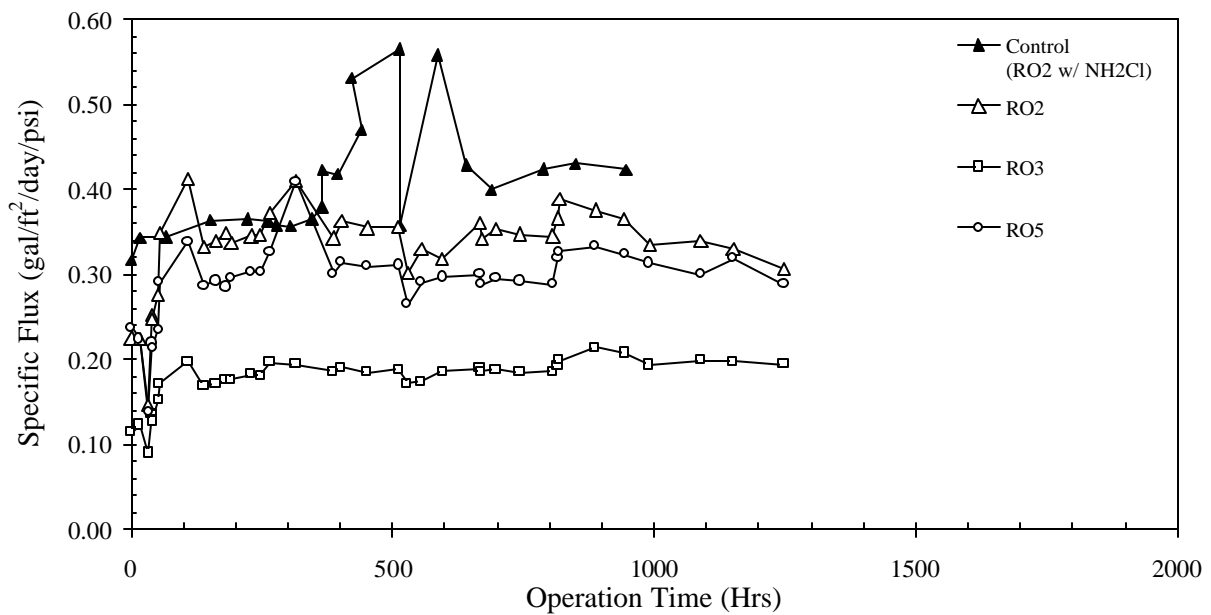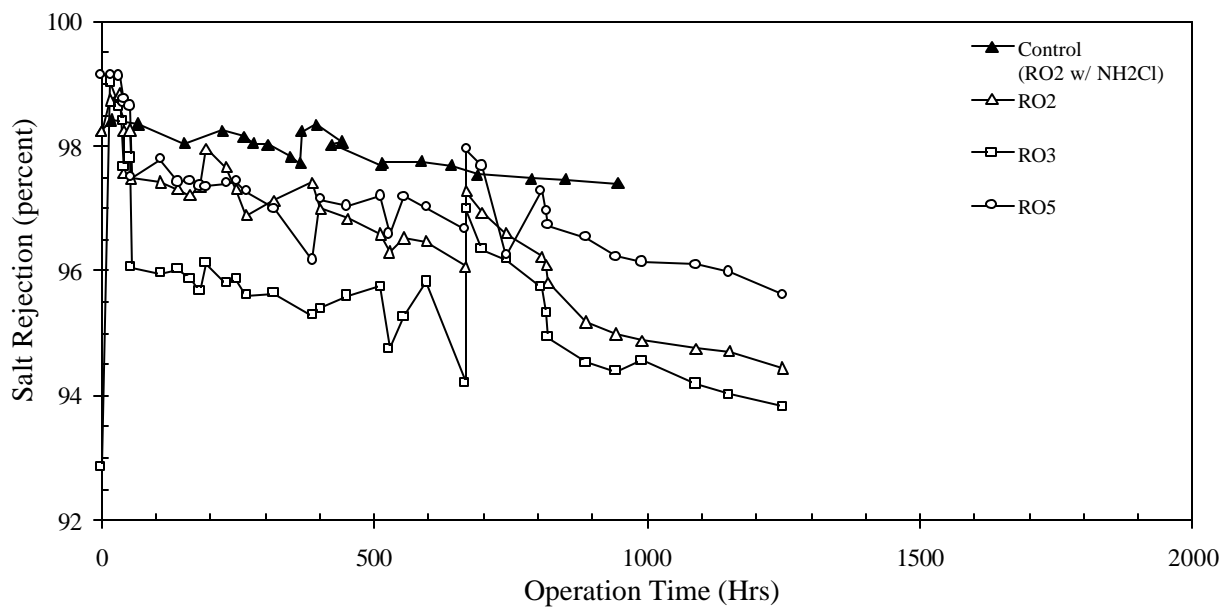Figure 27. Polymer structure of reverse osmosis membranes: (a) cellulose acetate and (b) polyamide

Figure 28. Specific membrane flux using Robert F. Skinner Filtration Plant effluent with ferric chloride with and without chloramines

Figure 29. Salt rejection using Robert F. Skinner Filtration Plant effluent with ferric chloride with and without chloramines
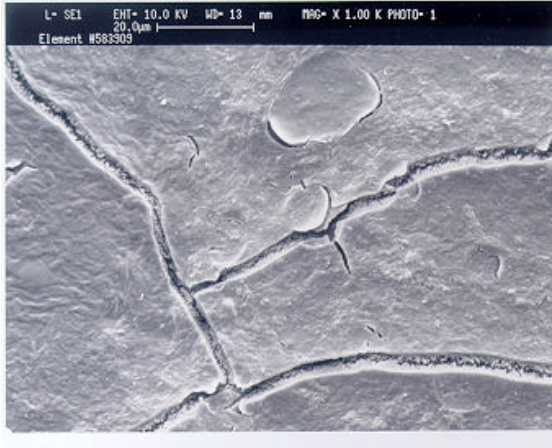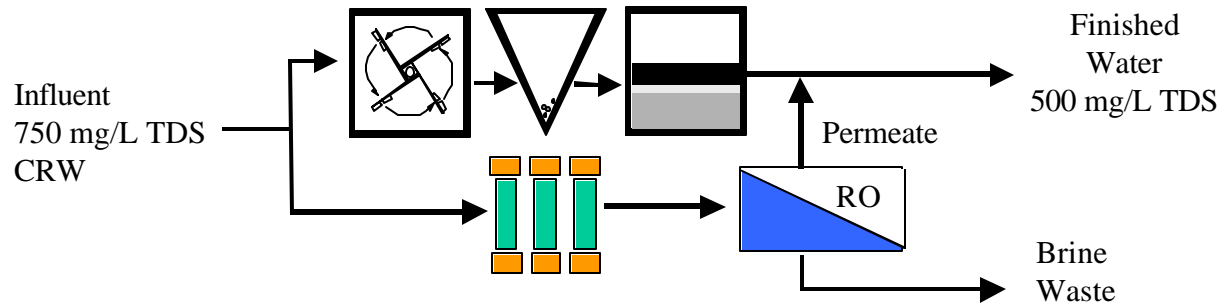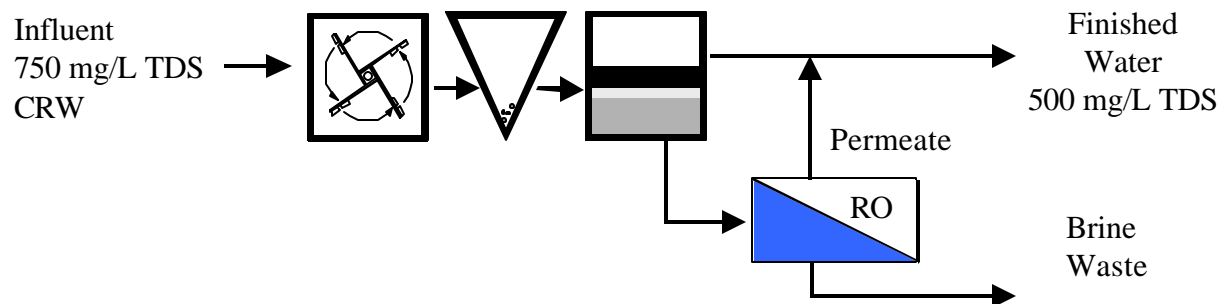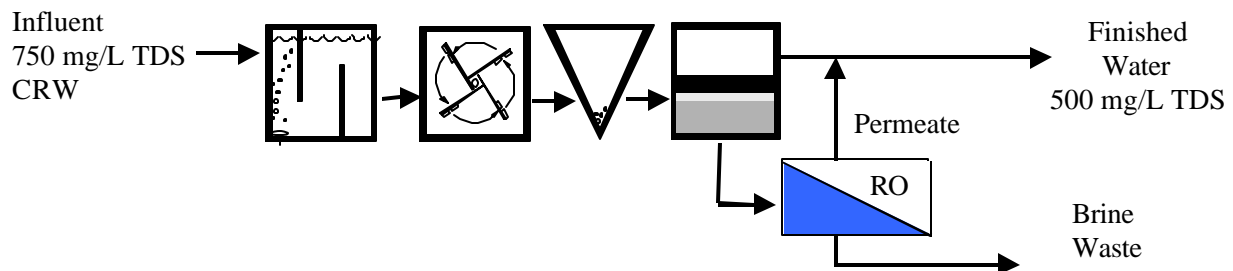
Figure 30. SEM micrographs of fouled reverse osmosis membranes Robert F. Skinner Filtration Plant effluent with ferric chloride: (a) without chloramines; (b) with chloramines

(a) Conventional treatment with Split-flow MF/RO

(b) Conventional treatment with split-flow RO

(c) Conventional Treatment with ozone/biofiltration and split-flow RO

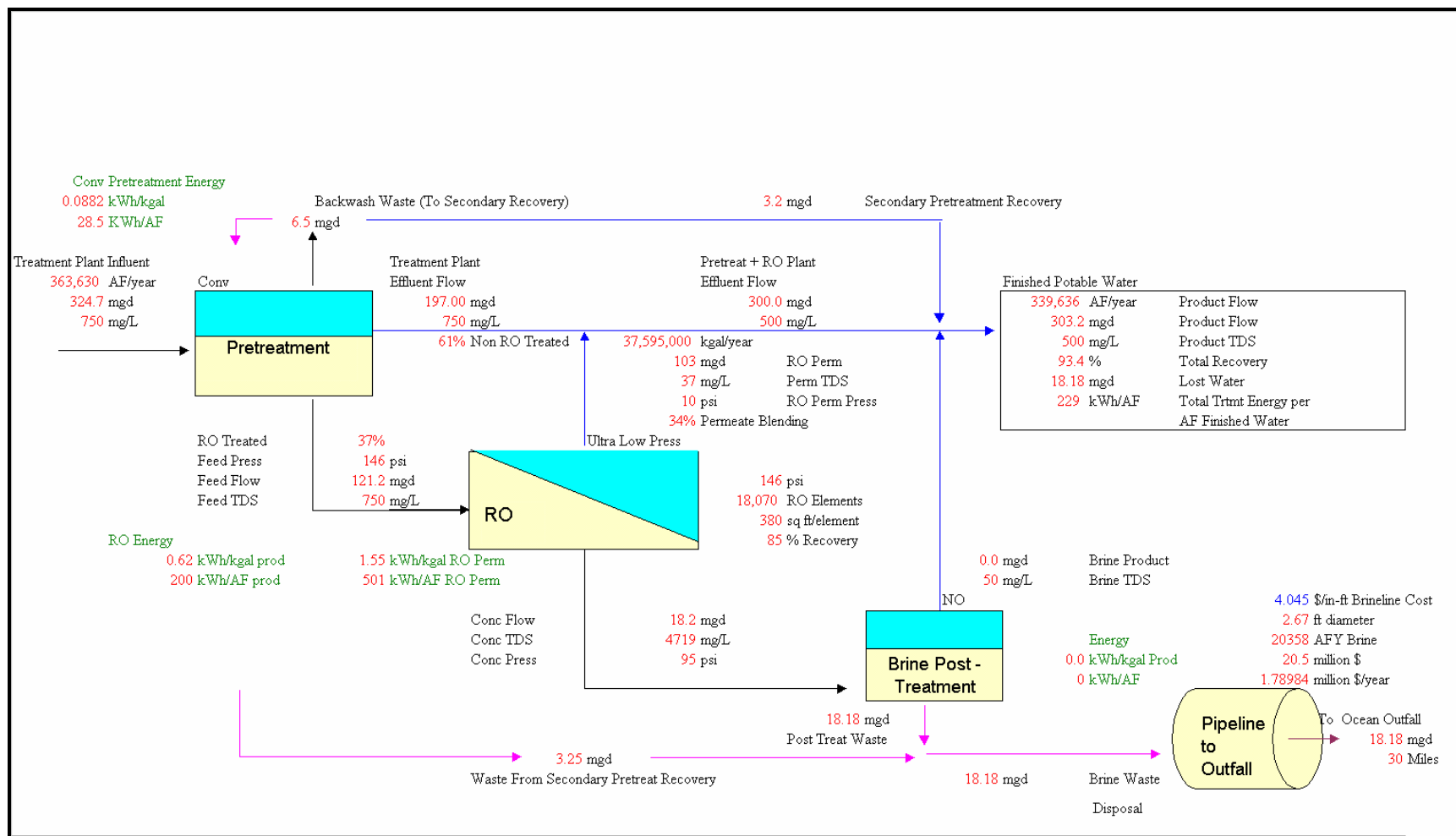Figure 31. Modeled split-flow treatment trains

Figure 32. Large-scale, split-flow desalination cost model

APPENDIX A

All water quality sampling was conducted by Metropolitan's staff. Inorganic and microbial analyses were analyzed at Metropolitan's Water Quality Laboratory in La Verne, Calif. The water quality constituents were analyzed according to the methods described below. *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA, and WEF 1998) was referenced for sample analysis wherever possible.

Inorganic Constituents

Alkalinity and Hardness were analyzed by titration according to Standard Methods 2320B and 2340C (APHA, AWWA, and WEF 1998).

Total Dissolved Solids (TDS) was measured using Standard Method 2540C (APHA, AWWA, and WEF 1998) or estimated from conductivity measurements.

Bromide, Chloride, Fluoride, Nitrate, and Sulfate were analyzed using a modified EPA Method 300.0 and a Dionex Model DX300 ion chromatograph. The minimum reporting levels (MRL) for each constituent (in mg/L) are: Br: 0.02, Cl: 2.0, F: 0.02, NO_3: 0.05, and SO_4: 4.0.

Silica levels were determined according to Standard Method 4500-Si D (APHA, AWWA, and WEF 1998) using a Shimadzu UV-2401PC ultraviolet/visible spectrophotometer.

Boron was measured using the Curcumin method as absorbance at 540 nm on a spectrophotometer against a standard curve using Standard Method 4500-B (APHA, AWWA, and WEF 1998).

Calcium, Magnesium, Potassium, Sodium were analyzed according to Standard Method 3111B (APHA, AWWA, and WEF 1998) using a Varian SpectrAA-300/400 atomic absorption spectrophotometer. The MRL for this method is 0.1 mg/L for each constituent.

Aluminum, Arsenic, Iron, Manganese, Barium and Strontium (trace metals) were analyzed according to EPA Method 200.8 using a Perkin Elmer Elan 6000 ICP-MS. MRLs for this method are as follows: Al: 5 µg/L, As: 0.5 µg/L, Fe: 20 µg/L; Mn: 5 µg/L; Ba: 5 µg/L, and Sr: 20 µg/L.

Total Organic Carbon (TOC) samples were analyzed by the ultraviolet/persulfate oxidation method (Standard Method 5310C, APHA, AWWA, and WEF 1998) using a Sievers 800 organic carbon analyzer. The MRL for this method is 0.05 mg/L.

Dissolved Organic Carbon (DOC) was defined by a filtration step involving a pre-washed 0.45 micron nylon membrane filter. DOC samples are analyzed by the ultraviolet/persulfate oxidation method (Standard Method 5310C, APHA, AWWA, and WEF 1998) using a Sievers 800 organic carbon analyzer. The MRL for this method is 0.05 mg/L.

Ultraviolet Light (UV) samples were analyzed at 254 nm using a Shimadzu UV-2401PC ultra-violet/visible spectrophotometer according to Standard Method 5910 (APHA, AWWA, and WEF 1995). Samples were filtered through a prewashed 0.45-µm Teflon membrane to remove turbidity which can interfere with UV measurement.

Free and Total Chlorine was measured using Standard Method 4500-Cl G (APHA, AWWA, and WEF 1998). For all free chlorine samples, 200 µl of 0.03 N thioacetamide solution per 10 mL of sample was added to control for interference by monochloramine.

Microbacteriological Methods

Heterotrophic Plate Count (HPC) bacteria were identified and enumerated using the R2A membrane filtration technique (plating in triplicate). R2A plates are incubated at 28ºC for 7 days, according to *Standard Methods* (APHA, AWWA, and WEF 1998).

Total Coliforms and *E. Coli.* were identified and enumerated according to *Standard Methods* (APHA, AWWA, and WEF 1998). Pretreatment influent and RO concentrate samples were

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analyzed using multiple tube fermentation methods and pretreatment effluent and RO permeate streams were analyzed using the membrane filtration option per *Standard Methods*.

APPENDIX B

In order to assess the performance of the pretreatment and salinity reduction steps, several key values were calculated based on raw process data. These calculated values include silt density index (SDI) for the pretreatment step and specific normalized flux, salt passage, and energy consumption for the RO system. These values were calculated using the following methods:

Specific Ultra Violet Light Absorbance at 254 nm (SUVA) was calculated by dividing the measured UV light absorbance at 254 nm (m^{-1}) by the measured TOC (mg/L) and multiplying by 100.

Silt Density Index (SDI) was measured using the method described by the American Society for Testing and Materials (ASTM) method D4189-82. The initial time (t_o) and the time after 15 minutes of continuous flow (t_{15}) to collect 500 ml through a 0.45 μm Millipore filter (Type HA, Millipore Corp., Bedford, Mass.) at 30 psig were measured. SDI was calculated using Equation 2.1:

$$SDI = \left[\frac{1 - \dfrac{t_o}{t_{15}}}{15} \right] * 100$$

where t_o = initial time in seconds to collect 500 ml

t_{15} = time in seconds to collect 500 ml after 15 minutes

Specific flux was calculated by the following equations:

Specific Flux = $(T_{Corr} * Q_{Permeate})/(a * P_{net})$ [gal/ft^2/day/psi]

where: T_{Corr} = Feed Temperature correction factor

$T_{Corr} = e^{(U* ((1/T) - (1/298))}$

where: U = 3100 for Koch Fluid Systems ULP-TFC membranes

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$$T = \text{Measured temperature [°C]}$$

$$Q_{Permeate} = \text{Permeate flow [gal/day]}$$

$$a = \text{Membrane surface area [ft}^2\text{]}$$

$$P_{Net} = P_{Feed} - \Delta\pi - \Delta P_{Hydraulic} - P_{Permeate} \quad \text{[psi]}$$

where: $\Delta\pi = \text{Differential osmotic pressure [psi]}$

$$\Delta\pi = 0.01 * (\Omega_{Average} - \Omega_{Permeate}) * (K_{Feed} + K_{Brine})/2$$

where: $K = \text{Conversion factor from conductivity to TDS [(mg/L)/(µS/cm)]}$
$\Omega = \text{Conductivity [µS/cm]}$

Salt rejection was calculated by the following equation:

Salt rejection = [1-(permeate TDS/feed TDS)] x 100